8-2004

Air Toxic Emissions Distribution and Performance Analysis of the CMAQ Air Toxic Model - A Case Study of Houston Area, Texas

Ramesh Ramachandran Gopal
University of Tennessee, Knoxville

To the Graduate Council:

I am submitting herewith a thesis written by Ramesh Ramachandran Gopal entitled "Air Toxic Emissions Distribution and Performance Analysis of the CMAQ Air Toxic Model - A Case Study of Houston Area, Texas." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

Joshua Fu, Major Professor

We have read this thesis and recommend its acceptance:

Terry Miller, Wayne Davis

Accepted for the Council:
Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

To the Graduate Council:

I am submitting herewith a thesis written by Ramesh Ramachandran Gopal entitled "Air Toxic Emissions Distribution and Performance Analysis of the CMAQ Air Toxic Model – A Case Study of Houston Area, Texas". I have examined the final paper copy of this thesis for form and content and recommend that it be accepted in partial fulfillment on the requirements for the degree of Master of Science, with a major in Environmental Engineering.

Joshua Fu, Major Professor

We have read this thesis
and recommend its acceptance:

Accepted for the Council:

Vice Chancellor and
Dean of Graduate Studies

Air Toxic Emissions Distribution and Performance Analysis of the CMAQ Air Toxic Model – A Case Study of Houston Area, Texas

A Thesis Presented for the Master of Science Degree

The University of Tennessee, Knoxville

Ramesh R. Gopal

August 2004

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my major professor, Dr. Joshua Fu. His mentorship and support helped me to not only complete my project, but also laid a foundation on which I can build my career as a professional. I wish to thank my committee members, Dr. Terry Miller and Dr. Wayne Davis, whose insights and time were invaluable. The members of my committee made my studies worthwhile and I am thankful for the opportunity to have been associated with such an extraordinary group of educators. I also want to acknowledge the University of Houston and the US Environmental Protection Agency for funding my research work and Dr. William Hutzell (EPA) for providing the air toxic model. I also wish to thank Mr. Ronald Thomas and Dr. Tom Porter from the Texas Commission on Environmental Quality, Dr. Daewon Byun from the University of Houston, Ms. Madeleine Strum from the EPA, and Mr. Prakash Doraiswamy from the University of Tennessee for all the support they provided. I want to give a special thanks to my parents, Ramachandran and Kousalya Gopal, for their love and support.

ABSTRACT

Air quality models have been used in the past to predict the ambient air toxic concentration but CMAQ air toxics model, used in this thesis, is the first air quality model, which accounts the toxic chemical reactions in the ambient atmosphere. The main objective of this thesis was to analyze the distribution of air toxics emission in the Houston region, Texas using an emission processing tool and to determine the performance of the advanced air toxics model (CMAQ) used. Each year large amount of air toxics are emitted in the state of Texas, particularly in the Houston region. A study on the hourly distribution of major toxics species emitted in the region would help the emission reduction policy makers to focus on the counties and areas within the counties which emit large amount of toxics in the region. The Texas toxic inventory and the national emission inventory were used as the inventory input for this study. The inventory emissions were processed using an EPA developed emission processing tool and the output from the tool was used to analyze the distribution of toxic emissions in the region. The latest air toxic model developed by the EPA is exclusively developed for air toxic species. The model has a detailed mechanism for chemical speciation in the atmosphere and has the ability to process most of major air toxic species. The output from the processing tool was also used to study the performance of this latest third generation air toxics model. The model was used to predict the concentration of major air toxics species for the year 2000 and the predicted concentration was compared with the monitored values in the region. A detailed analysis on the performance of the model was made and a conclusion on the effectiveness of the model was drawn.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Overview of Air Toxics

Air toxics are pollutants emitted in the atmosphere that are known or suspected to cause cancer or other serious health problems (EPA - 452/K-00-002, 2000). When people are exposed to toxic air pollutants at sufficient concentrations and duration, they have an increased chance of developing cancer or experiencing other serious health effects (ATW (Air Toxics Website)-intro, 2004). These health effects include damages to the immune, reproductive, respiratory, and neurological systems (ATW-intro, 2004). Certain toxic pollutants like mercury get deposited on the soil or surface water, where they are taken up by plants and ingested by animals and are ultimately magnified up the food chain (ATW-intro, 2004). A number of toxic species are also emitted in the form of particulates or as VOC, which form ground level ozone or smog (Air-Trends, 95). In 1990 the US EPA identified a total of 188 hazardous air pollutants under Clean Air Act and set regulations to control the emission of these species (Rosenbaum, 99). Before 1990 EPA set standards for each toxic species based on particular health risk (EPA - 452/K-00-002, 2000). This approach proved difficult and wasn't effective in controlling emissions (EPA - 452/K-00-002, 2000). In 1990, the Clean Air Act implemented a "technology based" and "performance based" approach to significantly reduce air toxics emissions from major sources (EPA - 452/K-00-002, 2000). Under the technology based approach MACT or "Maximum Achievable Control Technology" standards were set based on emissions levels that are already being achieved by lower emitting and better-controlled

sources in a facility (EPA - 452/K-00-002, 2000). By implementing this approach it was ensured that the facilities have cleaner processes and good emission controls and are relatively not disadvantaged to competitors with poorer controls (EPA - 452/K-00-002, 2000). In reality the MACT standards set by EPA have not worked in all the states, because MACT focused on point sources and in a number of states toxics are mainly emitted by mobile and area sources. The Houston Metropolitan region, which has significantly higher levels of toxics in the air than any other city in the USA, is one such example (Hamilton, 96). According to the 1993 Toxic Release Inventory the Houston area contributes almost half of the toxics emissions in Texas (Hamilton, 96).

1.2 Air Quality Modeling

Air quality modeling is done to predict the impact of pollutants released in the atmosphere on the surrounding regions based on weather, topography, and other factors (APCD, 2004). The models used simulate the atmospheric conditions and behavior of the region under study (Mid-Atlantic Air Protection, 2003) and the results obtained provide important information to decision makers, businesses, and the general public (APCD, 2004). The model output varies with input parameters like meteorological conditions, physical characteristics of the pollution source, and the surrounding topography (APCD, 2004). The photochemical grid models can be used to simulate emissions and chemical changes of a certain pollutant, all over the region under consideration, and predict the pollutant concentration over several days (APCD, 2004). The air quality models are used to perform two major tasks; the first is to predict pollutants concentrations or deposition estimates at almost all locations and second is to

predict the impact of new sources before they are built and also to determine the effects of any pollution controls before they are actually implemented (Mid-Atlantic Air Protection, 2003). Concentration modeling is also used to predict the health risk of toxic air contaminants and simulate accidental releases of hazardous materials in to the atmosphere. Typically air quality models are used in regulatory purposes, policy support, public information and scientific research (NILU, 2001).

1.3 Research Objective

In this thesis an advanced air toxics model called CMAQ air toxics model was used for the first time to model ambient air toxics concentration in the Houston region, Texas. Air quality models have been used in the past to predict the ambient air toxic concentration, but CMAQ air toxics is the first air quality model which accounts the toxic chemical reactions in the ambient atmosphere. The main objective of this thesis was to analyze the distribution of air toxics emission in the Houston region, Texas (Houston city is located in Harris County) using an emission processing tool and to determine the performance of the air toxics model (CMAQ) used. Each year large amount of air toxics are emitted in the state of Texas, particularly in the Houston region. According to the 1993 toxic release inventory, the eight counties of the Houston region emitted more toxics in the atmosphere than the entire state of Illinois, which (Illinois) was ranked tenth at that time (Hamilton, 96). A study on the hourly distribution of major toxics species emitted in the region would help the emission reduction policy makers to focus on the counties and areas within the counties which emit large amount of toxics in the region. The Texas toxic inventory and the national emission inventory were used as the inventory input for

this study. The inventory emissions were processed using an EPA developed emission processing tool and the output from the tool was used to analyze the distribution of toxic emissions in the region. Air toxics have been modeled in the past with two-dimensional models or three- dimensional models, which were primarily developed for criteria pollutants and were later modified to accommodate air toxics. These models predicted toxic species concentration with little or no emphasis on chemical speciation mechanisms. The latest air toxic model developed by the EPA is exclusively developed for air toxic species. The model has a detailed mechanism for chemical speciation in the atmosphere and has the ability to process most of major air toxic species. The output from the processing tool was also used to study the performance of this latest third generation air toxics model. The model was used to predict the concentration of major air toxics species for the year 2000 and the predicted concentration was compared with the monitored values in the region. A detailed analysis on the performance of the model was made and a conclusion on the effectiveness of the model was drawn.

CHAPTER 2

LITERATURE REVIEW

2.1 Air Toxics

2.1.1 Background

Air toxic pollutants, also known as hazardous air pollutants, are those species that are known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects, or undesirable environmental effects. Examples include benzene, found in gasoline; perchloroethylene released from some dry cleaning facilities; and methylene chloride, used as a solvent and paint stripper by a number of facilities (ATW-intro, 2004). Toxic air pollutants include both organic and inorganic chemicals, volatile and semi-volatile organic compounds, and metals. Once emitted in the environment, air toxic species may occur as gases, vapors, or as liquid droplets or solid particles. Some emitted air toxics retain their original chemical composition for long periods of time, while others react to form different chemical compounds (MPCA 2/16/01, 2001). The EPA, in collaboration with various state, local, and tribal governments, is working to reduce the release of 188 hazardous air pollutants into the atmosphere (EPA - 452/K-00-002, 2004).

2.1.2 Health Effects

People, when exposed to air toxic pollutants at sufficient concentrations and durations develop an increased chance of getting cancer or other serious health effects. The ill effects include damages to immune, respiratory, neurological, reproductive, development,

and other health systems (ATW-intro, 2004). When human beings are exposed to high levels of toxic species, a range of serious health effects occur. Examples of these serious health effects are: harm to specific organs, such as the liver, kidney, bones, heart, skin, etc., or to systems, such as the nervous, blood forming, respiratory, and immune systems. Minimum chemical exposure, which will result in a specific effect, depends on the chemical and particular effects. Certain effects are very apparent, while others, like behavioral changes or slight changes in blood chemistry, are more subtle and difficult to measure and are difficult to be identified in toxicity tests (MPCA 2/16/01, 2001). The various ways by which people are exposed to air toxic pollutants are by inhaling contaminated air, consuming contaminated food products such as fish, meat, etc., drinking toxic contaminated water, making skin contact with contaminated soil, dust, and water (ATW (Air Toxics Website)-intro, 2004).

In 1999, EPA developed a list of 33 toxic species, which pose the greatest threats to public health in urban areas. The list was based on emissions from all the four (point, area, mobile and non-road) major source categories (ATW-urban, 2004). The 33 species are listed in Table1.

In this thesis 15 of the 33 listed urban air toxics were considered for analysis. These fifteen species were selected based on both the ill effects caused by them to the human health and their emission trends in the region under consideration. The EPA follows a cancer classification system to determine the level of risk posed by a particular toxic species. A weight-of-evidence procedure, which determines the ability of a chemical to cause cancer in humans, is used to make this classification.

Table 1 EPA's list of 33 Urban Air Toxics (ATW-urban)

Acetaldehyde	Acrolein
Acrylonitrile	Arsenic compounds
Benzene	Beryllium compounds
1,3- Butadiene	Cadmium compounds
Carbon tetrachloride	Chloroform
Chromium compounds	Coke oven emissions
Dioxin	Ethylene dibromide
Propylene dichloride	1,3- Dichloropropene
Ethylene dichloride	Ethylene oxide
Formaldehyde	Hexachlorobenzene
Hydrazine	Lead compounds
Manganese compounds	Mercury compounds
Methylene chloride	Nickel compounds
Polychlorinated biphenyls	Polycyclic organic matter
Quinoline	1,1,2,2- tetrachloroethane
Perchloroethylene	Trichloroethylene
Vinyl chloride	

The classification is as follows

- Group A - Human carcinogen
- Group B
    - B1--Probable human carcinogen, very limited human data are available
    - B2--Probable human carcinogen, sufficient evidence in animals and insufficient or no evidence in humans
- Group C--Possible human carcinogen
- Group D--Not classifiable as to human carcinogenicity
- Group E--Evidence of non carcinogenicity for humans

A description of the health effects caused by the toxic species considered in this thesis, along with the cancer group to which each species belong to, is given in Table 2.

The health effect details were obtained from EPA's "Health Effect Notebook for Hazardous Air Pollutants, 2004".

2.1.3 Sources of Emissions

Scientists estimate that millions of tons of toxic pollutants are emitted in the atmosphere each year. Most air toxics are emitted by human-made sources, this includes mobile sources (cars, buses, trucks) and stationary source (factories, refineries, power plants), as well as indoor sources (building materials). Some air toxic species are also emitted in large amount by natural sources like volcano, forest fires etc. Typical emissions from stationary sources constitute almost one half of all manmade air toxics emissions (EPA - 452/K-00-002, 2000). The stationary sources are mainly divided into two types: major sources and area sources.

Table 2 Health effects caused by toxic species considered

Toxic Species	Health Effect	Cancer Classification
Acetaldehyde	Irritation of eye, skin and respiratory tract; elevates blood pressure, depresses respiratory rates	Group B2
Acrolein	Death (when exposed at high levels); Lung problems; respiratory congestion; skin, eye, nose, and throat irritation	Group C
Acrylonitrile	Membrane irritation, headaches, nausea, nervous irritability; Kidney irritation, mild jaundice, leukocytosis	Group B1
Benzene	Leukemia; Blood disorder; Skin, eyes, and respiratory track irritation; Drowsiness, dizziness, headaches and vomiting;	Group A
Butadiene	Leukemia; Neurological effects, eye irritation; heart diseases; liver disorder;	Group B2
Carbon tetrachloride	Damages liver, kidney, and central nervous system;	Group B2
Chloroform	Central Nervous System depression; death (when exposed at high levels); liver disorder; kidney tumor.	Group B2

Table 2 continued

Toxic Species	Health Effect	Cancer classification
Ethylene Dibromide	Severe skin irritant, causes depression, affects kidney and liver	Group B2
Ethylene oxide	Neurological disorders; nausea, vomiting; eyes and skin irritation; cataracts; miscarriage; stomach and pancreatic cancer	Group B1
Methylene chloride	Affects Central Nervous System (CNS), liver, kidney, cardiovascular system; causes acute toxicity in the body	Group B2
Perchloroethylene	Irritation of upper respiratory tract, kidney dysfunction, neurological effects; affects kidney, liver, central nervous system; affects reproductive system	Group C
Propylene Dichloride	Affects gastrointestinal systems, blood, liver, kidney, respiratory and central nervous system	Group B2
Trichloroethylene	Affects central nervous system, lungs, kidney, and heart	

Table 2 continued

Toxic Species	Health Effect	Cancer Classification
Vinyl chloride	Ill effects on CNS; eyes and respiratory track irritation; loss of conscious; lung and kidney irritation; liver damage; affects reproductive system; liver cancer	Group A
Ethylene Dichloride	Affects nervous system, causes cardiac arrhythmia, eye irritation; affects liver and kidneys	Group B2

Major sources are defined as sources that release 10 tons per year of any of the listed 188 air toxic pollutants, or 25 tons per year of a mixture of air toxics (ATW –Pollutants and Sources, 2004). These sources emit air toxics from emission stacks and vents, fugitive process emission, equipment leaks, material transfer and handling, or accidental releases (CDEP, 1999). Area sources are defined as sources that release less than 10 tons per year of a single air toxic, or less than 25 tons per year of a combination of air toxics (ATW – Pollutants and Sources, 2004). These sources normally consist of smaller-size facilities like dry-cleaners, gas stations, small print shops, auto body shops, electroplaters, and small manufactures that release fewer quantities of toxic pollutants in the air. Though the emissions from each area source are relatively small, the collective emissions from area sources generate significant health risks, particularly if a large number of area sources are

located in regions with high population. In 1990, the EPA estimated that area sources form 31% of all man-made air toxic emissions in the United States. Mobile source emission includes emissions from automobiles, trucks and buses. Toxic pollutants are emitted by mobile sources due to incomplete combustion of fuel and evaporation of fuel. Although great gains were made in fuel economy and efficacy of air pollution control equipment over the past twenty years, in 1990 EPA estimated that mobile sources contribute 39% of all man-made air toxic emissions in the United States (CDEP, 1999). Non-road sources is a category of mobile sources, which include equipment and off-road vehicles fueled with diesel fuel, gasoline, propane, or natural gas in the following sectors: recreational engines and vehicles (golf cart, snow mobile), construction equipment and vehicles, industrial equipment, lawn and garden equipment, farm equipment, commercial equipment (generators, pumps), logging equipment, airport service equipment and vehicles, railway maintenance equipment, aircrafts, marine vessels and locomotives (EPA-OTAQ, 2003).

2.1.4 Regulations

To this date no organization has developed a single complete list of toxic air pollutants, which are relatively of greater concern. Only partial lists were developed based on available, but often limited, information about the species toxic effects, amounts released to the air, and their measured ambient air concentrations. Before 1990 Clean Air Act Amendments Congress defined "hazardous air pollutants" as pollutants, which cause or contribute to air pollution, eventually resulting in an increase in mortality or an increase in serious irreversible illness. This definition was reframed in 1990 Clean Air Act

Amendments and was specific to 188 toxic chemicals. As per the Section 112(k) of the 1990 Clean Air Act Amendments, the US EPA conducted an urban scale assessment and identified a list of 33 Priority Air Toxics for the Integrated Urban Air Strategy. There are many factors, which restrict scientists' ability to identify all toxic pollutants of concern; these include lack of comprehensive toxicity information and exposure data (MPCA 2/16/01).

Prior to 1990, the Clean Air Act directed EPA to control toxic air pollutants emissions based on the risks each pollutant posed to human health. The main requirements of the act were to identity all pollutants that caused "serious or irreversible illness or death" and development of standards to reduce emissions of these pollutants to levels that offered a sufficient margin of safety for the public. While attempting to regulate air toxics during the 1970s and 1980s, EPA became involved in many legal, scientific, and policy debates over which pollutants to control and how stringently to regulate them. The arguments mainly focused on risk assessment methods and assumption, the amount of health risk data needed to justify regulation, analyses of the costs industry, and benefits to human health and environment. During this period, EPA was still developing methods to review risk. These methods were important tools that would be required to establish the scientific basis for making risk-based decisions about air toxics. Despite gaining valuable knowledge about risk assessment methods, the EPA found the chemical-by-chemical regulatory approach, an approach based solely on risk, difficult to implement. In the twenty year period, the EPA was able to regulate only seven toxic species (asbestos, benzene, beryllium, inorganic arsenic, mercury, radio nuclides, and vinyl chloride). Recognizing the limitations of a chemical-by chemical decision frame work

based exclusively on risk, and acknowledging the gaps in scientific and analytical information, Congress adopted a new approach in 1990, when the Clean Air Act was amended. Congress revised Section 112 of the Clean Air Act to mandate a more realistic approach to reducing emissions of toxic air pollutants. The approach has two components in it. In the first phase, EPA created regulations – MACT standards- necessitating sources to meet specific emission limits that are based on emissions levels already being achieved by many similar sources in the country. This new technology-based approach clearly produced real, measurable reductions in the initial stages itself. In the second phase, EPA applies a risk-based approach to review how these technology based emissions limits are reducing health and environmental risks. Based on this assessment, EPA may apply additional standards to deal with any important remaining, or residual, health or environmental risks. The approach for addressing remaining risks from air toxics was completed by the EPA in 1999. When developing a MACT for a specific source category, EPA observes the level of emissions currently being accomplished by the best-performing similar sources through clean processes, control devices, work practices, or other methods. These emission levels set a baseline, also known as MACT floor, for the new standard. The MACT standard set must at least achieve, throughout the industry, a level of emissions control equivalent to the MACT floor. The MACT floor is set differently for existing sources and new sources. In the case of existing sources, the MACT floor must equal the average emissions limitations currently attained by the best performing 12 percent of sources in that source category, if there are 30 or more existing sources. If there are lesser than 30 existing sources, then the

MACT floor must be equivalent to the average emissions limitation achieved by the best-performing five sources in the category.

In the case of new sources, the MACT floor must be equivalent to the level of emissions control achieved at present by the best-controlled similar source. As of August 2000, EPA has set 45 air toxics MACT standards under section 112 of the Clean Air Act Amendments. These standards have an effect on 82 categories of major industrial sources, such as chemical plants, oil refineries, aerospace manufactures, and steel mills, as well as eight categories of area sources, such as dry cleaners, commercial sterilizers, secondary lead smelters, and chromium electroplating facilities. It is estimated that when all the standards set are fully implemented air toxics emissions in the country will be reduced at the rate of 1.5 million tons per year, this is nearly equal to 15 times the reduction achieved before 1990. Some of the air toxics standards set have the added benefit of reducing ground level ozone and particulate matter. This reduction occurs as some air toxics are also smog causing volatile organic compound (benzene, toluene etc.) or particulate matter (chromium, etc.).

Also some of the technologies and practices developed to control air toxics reduce VOCs or particulate matter that are not on the listed 188 hazardous air pollutants (EPA - 452/K-00-002, 2000).

2.1.5 Emission Inventories

The US Environmental Protection Agency develops two separate inventories for air toxic emissions. These are the "Toxic Release Inventory" which is developed each year and the "National Emission Inventory", which is developed once every three years.

National Emission Inventory

EPA's Emission Factor and Inventory Group develop a national database of air emissions information with input from numerous state and local agencies, from tribes, and from industry. The database developed has information on stationary and mobile sources that emit criteria air pollutants and their precursors, as well as hazardous air pollutants. The inventory includes estimates of annual emissions, by source, of air pollutants in each area of the country, on an annual basis. The National Emission Inventory has emission estimates for all 50 states, the District of Columbia, Puerto Rico, and the Virgin Islands. Emission estimates for individual point sources, as well as county level estimates for area, mobile and other sources, are available at present for years 1985 through 1999 for criteria pollutants, and for years 1996 and 1999 for hazardous air pollutants. The data present in the national emission inventory (NEI) are used for air dispersion modeling, regional strategy development, regulation setting, air toxics risk assessment, and tracking trends in emissions over time. Before 1999, criteria pollutants emission estimates were maintained in the National Emission Trends (NET) database and air toxics pollutants estimates were maintained in the National Toxic Inventory (NTI) database. Beginning with 1999, criteria and HAP emissions data are being developed in a more integrated fashion in the National Emission Inventory (NEI), which replaces NET and NTI. The National Emission Inventory contains emission estimates for the 188 HAPs from stationary major and area sources and mobile sources, as defined in the Clean Air Act. The NEI for toxics is compiled from State and local HAP inventories, current databases related to EPA's Maximum Achievable Control Technology (MACT) programs to reduce HAP emissions, Toxic Release Inventory (TRI), emissions predicted by utilizing mobile

source methodology created by EPA's office of transportation and air quality, and stationary non-point source emission estimates generated using estimation factors and activity data (NEI background, 2004). The National Emission Inventory, developed once every three years, has a different inventory for each of the four types of sources. They are point source inventory, area source inventory, mobile source inventory and non-road source inventory.

Point source inventory

The main objective of the EPA in developing the point source NEI was to obtain facility specific data such as facility name, location, stack information, emissions and process descriptions. The first step in this process was to obtain facility-specific data from state and local air pollution control agencies, which are most likely to have detailed HAP inventory. Inventory data were also obtained from EPA's Emission standard division (ESD) for Maximum Achievable Control Technology (MACT) source categories. To create a complete point source NEI, TRI data were also used. The reason for including the TRI data to the local, state, ESD combined databases was to make sure all emission data for facilities that report to TRI are included in the NEI. The facilities that did not have stack parameter details were supplemented with default stack parameters. These default stack parameters were generated by Emission Factor and Inventory Group (EFIG), utilizing data from NEI99 version 1, for more than 3000 SCCs. The supplementation was done to make the point source inventory suitable for exposure modeling (NEI 99- point source documentation, 2004).

Area Source Inventory

The 1999 area source NEI contains 449 source categories and 160 HAPs, cumulating to nearly 2.66 million county level records. The development of area source inventory is generally done in a sequential manner; it involves planning, gathering information, estimating emissions, analyzing state, local, tribal, and revised data and comments for incorporation, conducting quality control and checks and comparing emissions data for similar source categories that are in the point NEI. The planning phase focuses on recognizing the source category that could be used to predict emissions. The data for the inventory were obtained mainly from the Emission Factors and Inventory group, EPA's Emission Standard Division, Emission factors and activity data used by EFG and the previous version's area source NEI (NEI99 – area source documentation, 2004).

Mobile Source Inventory

EPA utilizes MOBILE 6.2 mobile source emission factor model to develop mobile source inventory for both criteria and toxic pollutants. In the case of criteria pollutants on-road emissions were calculated by multiplying an appropriate MOBILE 6.2 emission factor in grams per mile by the corresponding VMT in millions of miles. The estimated emissions include calculations by month, county, road type, and vehicle type. HAPs emissions were calculated in a similar method, but emission factors were calculated by season rather than month. To create VMT for the NEI, EPA relies on data supplied by the Federal Highway Administration (FHWA) and publicly available data from FHWA's Highway Statistics series (NEI – mobile source documentation, 2004).

Toxic Release Inventory

The Toxic Release Inventory is a publicly accessible database, which contains information on toxic chemical releases and other waste management activities reported each year by certain covered industry groups as well as federal facilities. This inventory was first developed in 1986 under the Emergency Planning and Community Right-to-Know Act and was later modified by the Pollution Prevention Act of 1990. The main objective of the TRI is to empower citizens, through information, to hold companies and local governments accountable in terms of how toxic chemicals are managed. The Toxic Release Inventory is complied by the EPA every year and it is made accessible to the public through various data tools like TRI Explorer and Envirofacts. The TRI program has significantly developed since its introduction in 1987. The EPA has issued rules to almost double the number of chemicals included in the TRI to roughly 650. Seven new industries have also been added to increase the coverage significantly beyond the original covered industries. A recent development is the reduction in the reporting thresholds for certain persistent, bioaccumulative, and toxic (PBT) chemicals in order to provide additional information to the public on these chemicals (TRI). A facility is required to report to TRI if it conducts manufacturing operations with in the Standard Industrial Classification (SIC) codes 20 through 39 or has 10 or more full time employees equivalent or manufactures or processes more than 25,000 pounds or otherwise uses more than 10,000 pounds of any listed chemical during the calendar year (TRI 2000 – executive summary).

2.1.6 Air Toxics Monitoring

Unlike criteria pollutants, EPA and states do not maintain an extensive nationwide monitoring network for air toxics. Though EPA, states, tribes, and local air regulatory agencies collect monitoring data for a number of air toxic species, both chemicals monitored and geographic coverage of the monitors vary from one state to another. EPA is collaborating with these regulatory partners to build upon the existing monitoring sites to develop a national monitoring network for a number of toxic air pollutants. The objective is to ensure that those compounds that pose the greatest risk are measured. In 2001, EPA began a pilot city monitoring project and is scheduled to include at least 12 months of sampling in four urban areas and six small city/rural areas. The main objective of this program was to help answer several important national network design questions (Air trends 2003). Figure 1 shows the recent EPA's air toxic monitoring station initiatives. Figure 2 represents the comparison of the risk posed by air toxic emissions in the region; Houston region is designated as a high risk region.

2.1.7 Air Toxics Emission Trend

In this section a detail examination of the toxic emissions trend, both on the basis of national emission inventory and toxic release inventory, is performed. The two inventories were treated separately due to the difference in the reporting time period and source categories. The national emission inventory is released once every three years and has emissions from all the four types of sources (point, area, non-road and mobile), while the toxic release inventory is released each year and has emissions from point sources only.

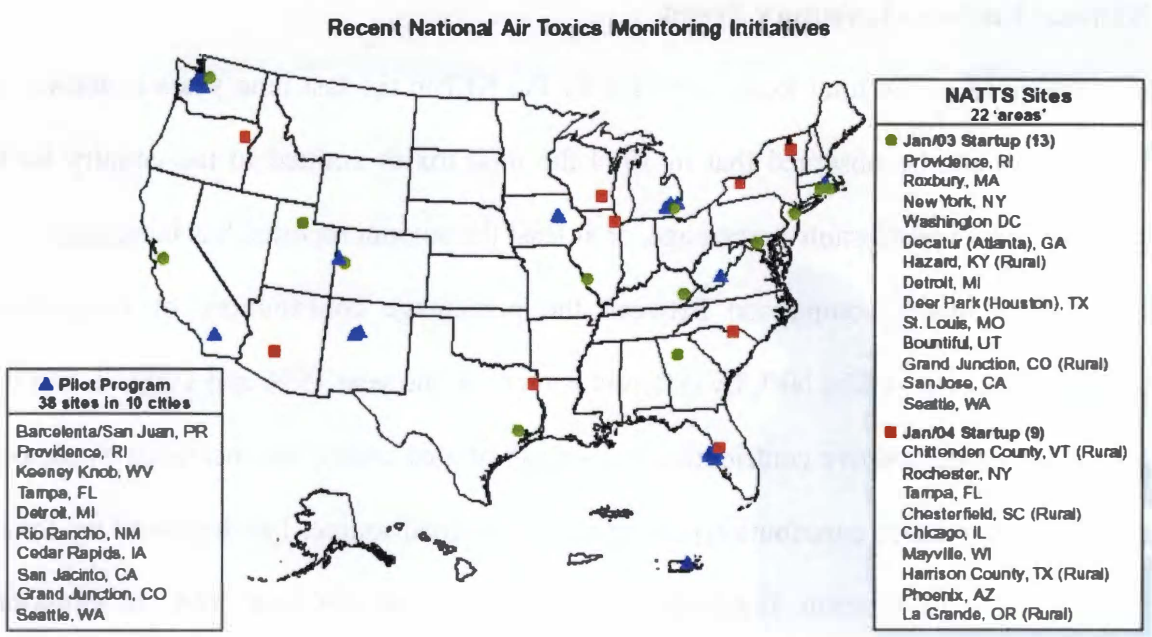


Figure 1 EPA's recent air toxics monitoring initiatives (Air trends report, 2003)

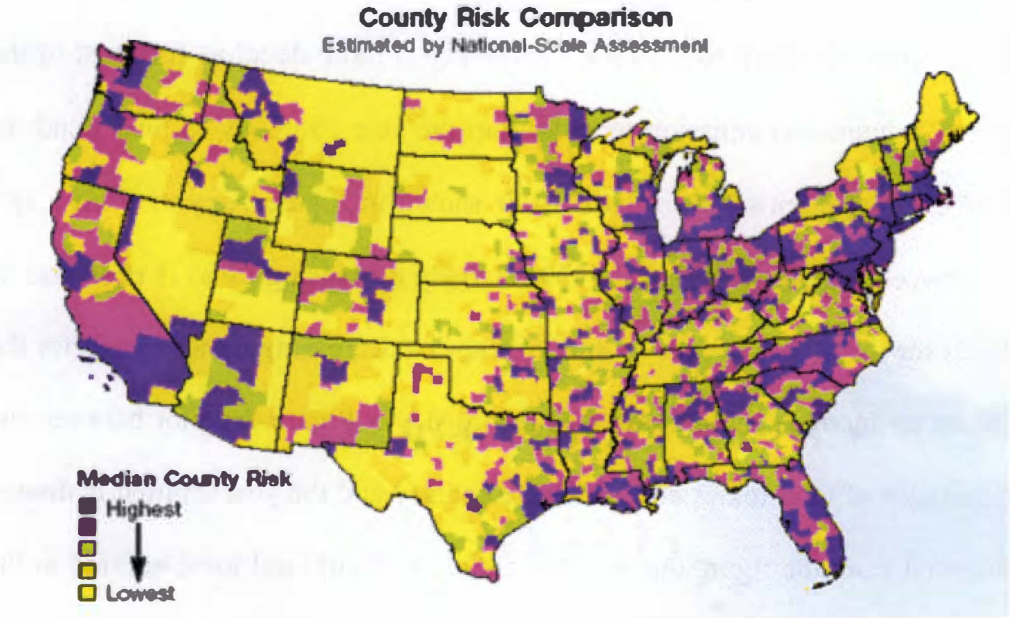


Figure 2 Comparison of risk posed by air toxics emission in the nation (Air Trends report, 2003)

National Emission Inventory Trend

A comparison of the total toxics reported by the NEI in the last nine years is shown in Figure 3; it can be observed that in 1999 the total toxics emitted in the country have increased by a considerable percentage, or at least the amount reported has increased.

Figure 4 shows a comparison between the percentage contribution, of total toxic emissions reported in the NEI, by different sources in the year 1996 and 1999. It can be observed that the relative contribution percentage of area source has increased by almost 7% while the relative contribution percentage of non-road sources has decreased by about five percent. In a recent Texas study it was found that the total VOC in emission inventories are under estimated by a factor of 2 to 10 for multiple sources and by a factor of 2 to 43 for single source emissions inventory (Brown, 2004).

Toxic Release Inventory - Trend

The analysis of emissions from toxic release inventory is more detail as for most of the toxic species EPA maintains emission records from the year 1988. A 13 year trend for the 1988 core chemicals emission in the USA is shown in Figure 5, apart from a few fluctuations between the years 1997 and 1999 a largely decreasing trend is observed. A similar analysis for the state of Texas (Figure 6) shows a decreasing trend, except for the year 1998 when an increase in emission was recorded. In Figure 7 a plot between the Texas's percentages of total toxics emitted in the country and the year emitted is drawn. It can be observed from the figure that in 1988 almost 8.5% of total toxic emitted in the country is from the state of Texas, this percentage has risen to almost 11% in 2001. A similar plot between Harris County's percentages of total toxics emitted in the state of

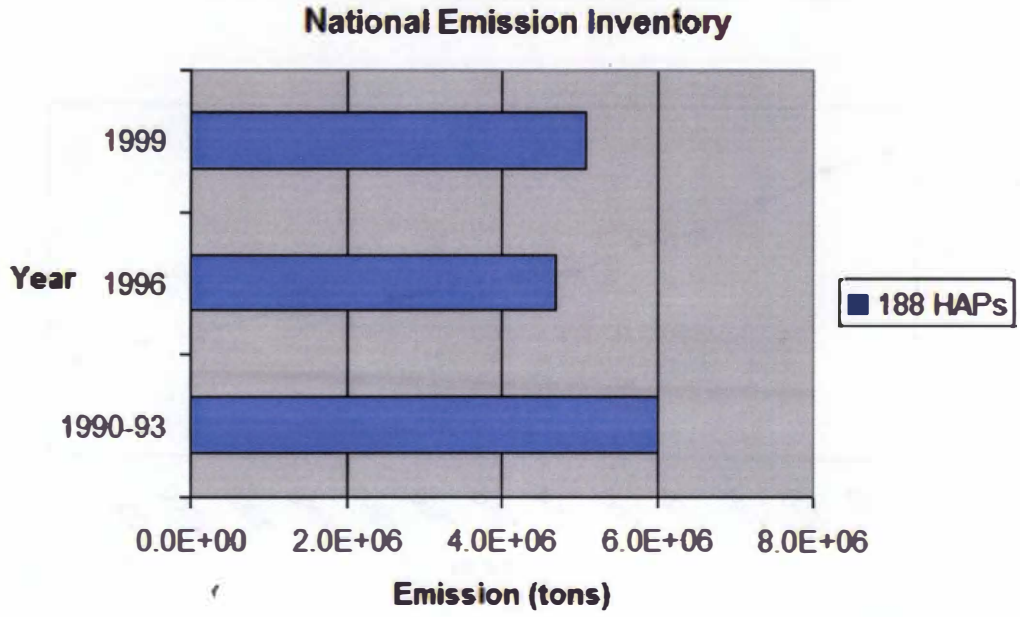


Figure 3 Emission trends of 188 HAPs listed by the EPA

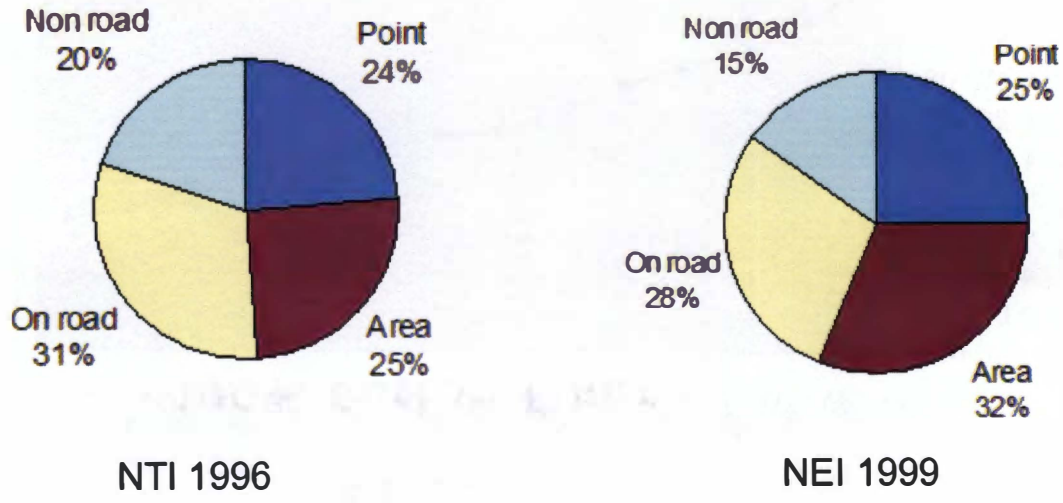


Figure 4 Source distributions of total air toxics emitted in the country (EPA)

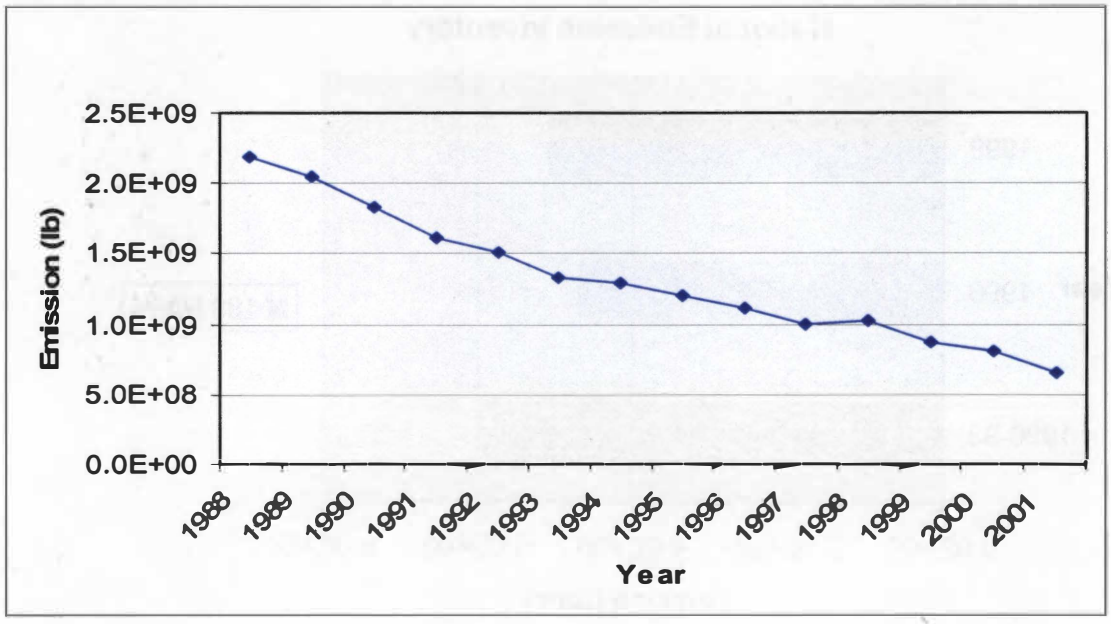


Figure 5 Toxic Release Inventory emissions (1988 Core Chemical) trend - USA

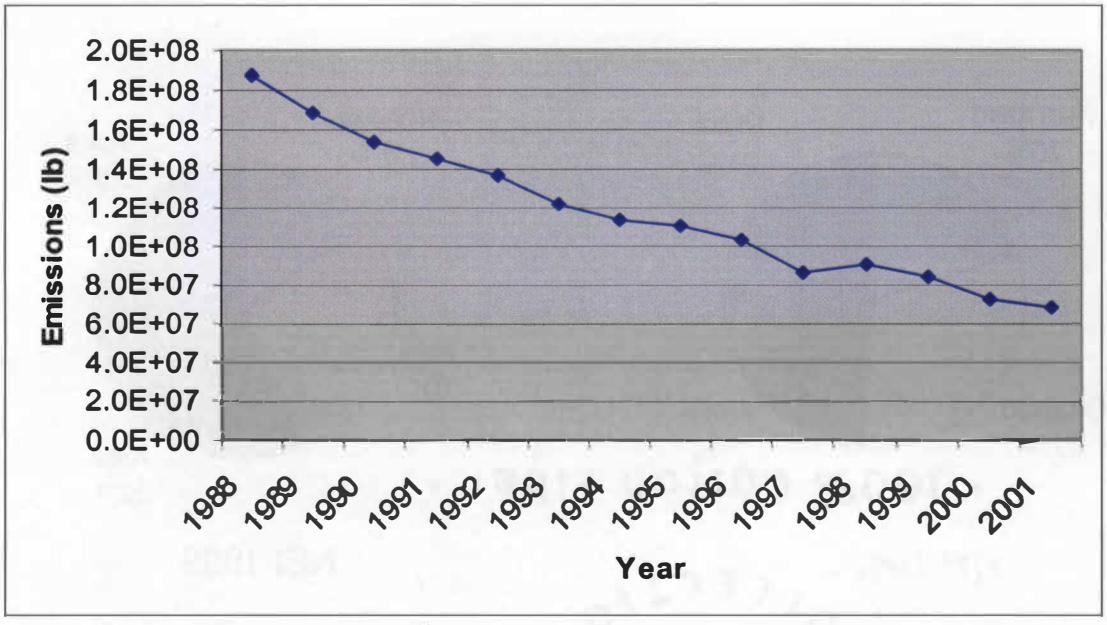


Figure 6 Toxic Release Inventory emissions (1988 Core Chemical) trend - Texas

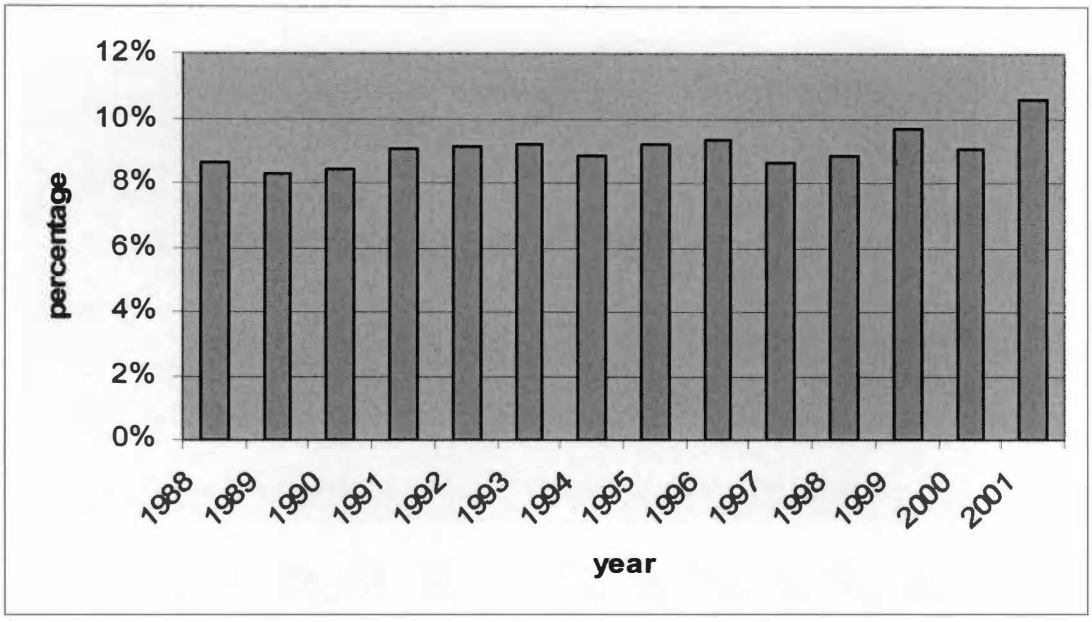


Figure 7 Percentage contribution of Texas to the total toxic emissions (TRI) in the US

Texas and the year emitted are shown in Figure 8, showing that Harris County has stayed essentially proportional to the state emission.

Emission trend of toxic species considered

The emission trends of the 15 toxic species considered for analysis in this thesis were plotted and are presented in this section. For each toxic species the 13-year emissions trend in the country, state (Texas) and the county (Harris) is plotted. All the emissions shown in this plot were obtained from toxic release inventory and hence all the discussions related to the trend apply to TRI database only. The following observations were made from the plot.

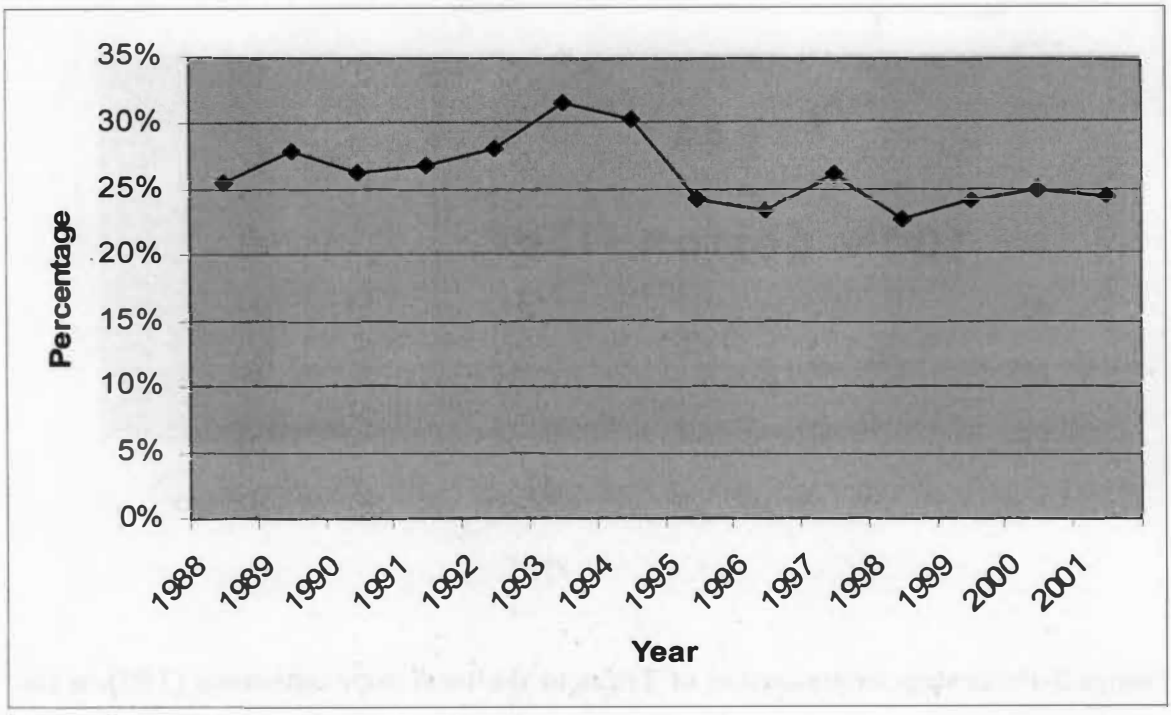
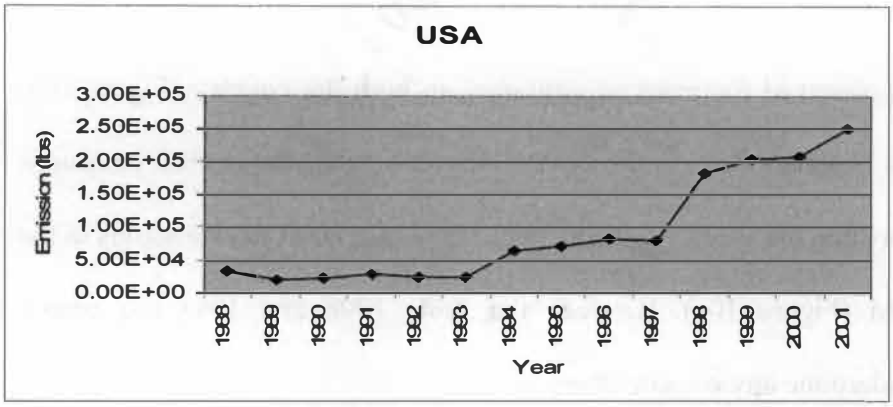


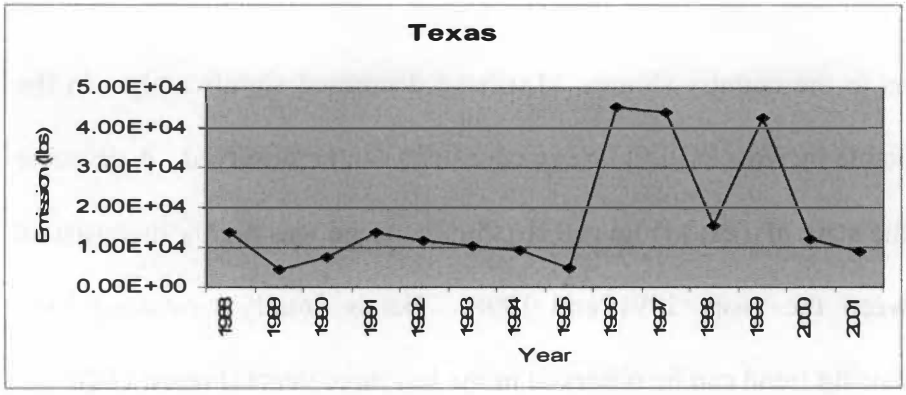
Figure 8 Percentage contribution of Harris County to the total toxic emissions (TRI) in Texas

Acrolein

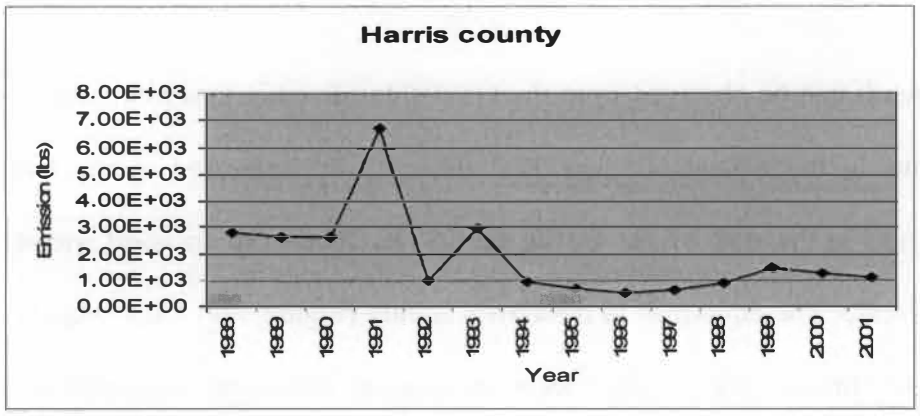
Acrolein emissions in the nation have increased significantly in the past 13 years, particularly between the years 1997 and 2001 (Figure 9a). The Texas state emissions of acrolein is inconsistent, though the total emissions have marginally decreased in the last thirteen years the emissions between the years 1995 and 1996 increased approximately by a factor of 4 (Figure 9b). Harris county acrolein emissions were highly inconsistent between the years 1990 and 1994; the overall emissions in the county have decreased (Figure 9c).



a)



b)



c)

Figure 9 Acrolein emissions trend from Toxic Release Inventory. a) USA b) Texas c) Harris County

Benzene

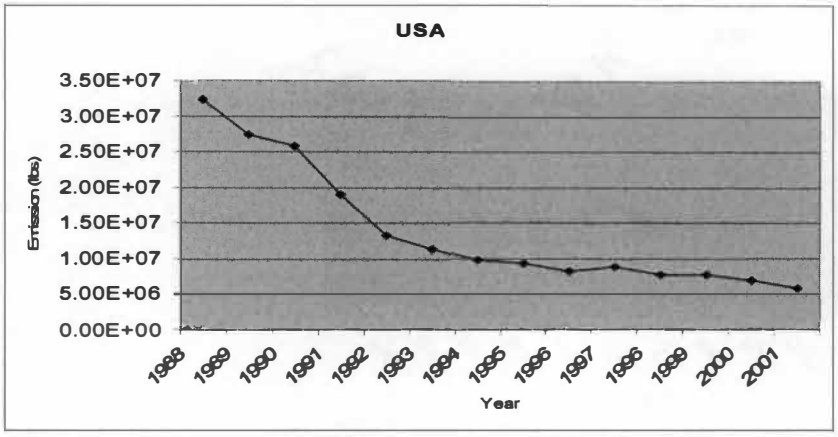
A decreasing trend is observed for benzene emissions in both the country (Figure 10a) and the state of Texas (Figure 10b). In the case of Harris County the overall emissions have decreased but between the years 1989 and 1991, 1998 and 2000 the emissions in the county have increased (Figure 10c). Between the years 1996 and 1998 the county emissions have not undergone any notable changes.

1, 3 Butadiene

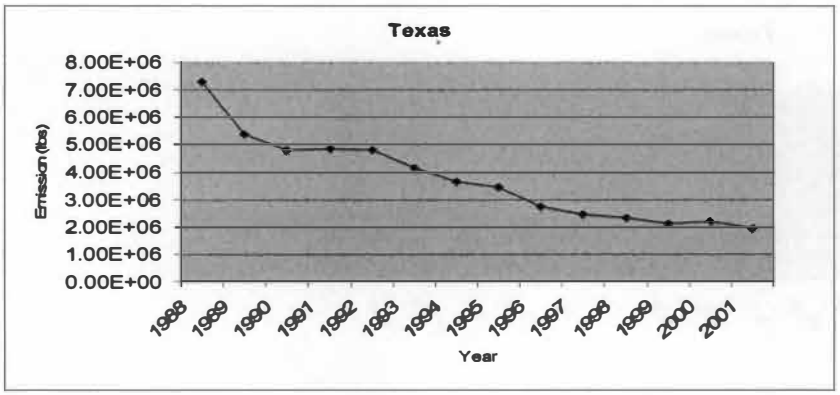
The overall emissions in the country (Figure 11a) have decreased significantly. In the last three years no notable increase or decrease in emissions can be observed. A decrease is also observed for the state of Texas (Figure 11b), but the trend was highly inconsistent and fluctuating between the years 1991 and 1998. Harris county emissions have decreased but an increasing trend can be observed in the last three years (Figure 11c).

Vinyl Chloride

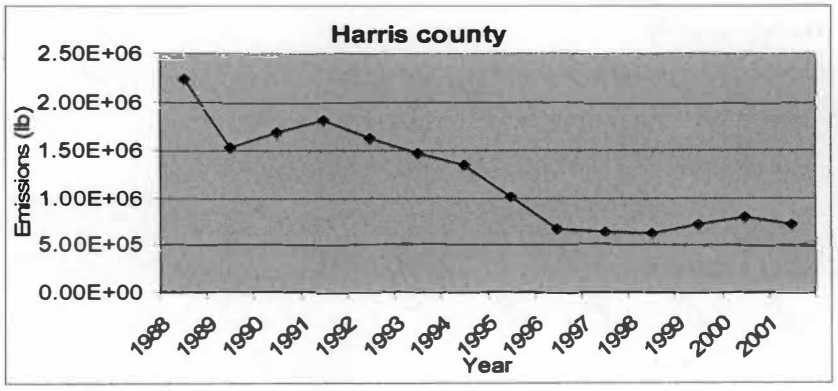
Three contrasting trends can be observed from the vinyl chloride emissions plot. While the overall emissions in the country (Figure 12a) have steady decreased in the last decade, emissions trend in the state of Texas (Figure 12b) have been inconsistent with a marginal overall increase. The emissions in the Harris county (Figure 12c) have steadily increased in the last thirteen years. Significant increase in emissions was recorded between the years 1990 and 1992.



a)

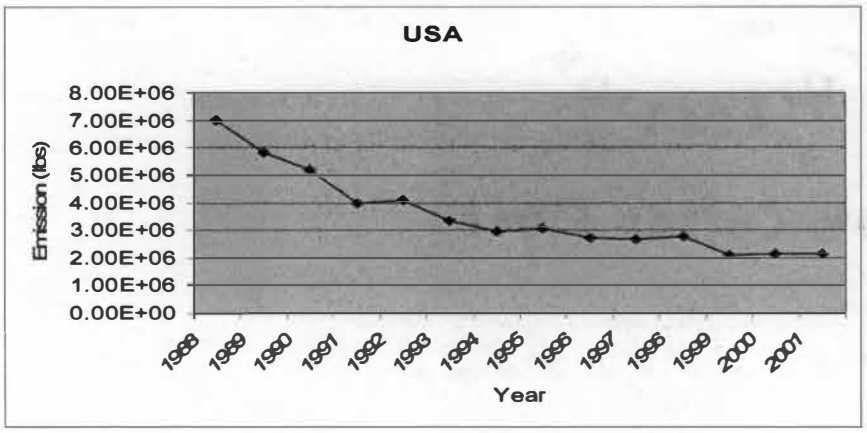


b)

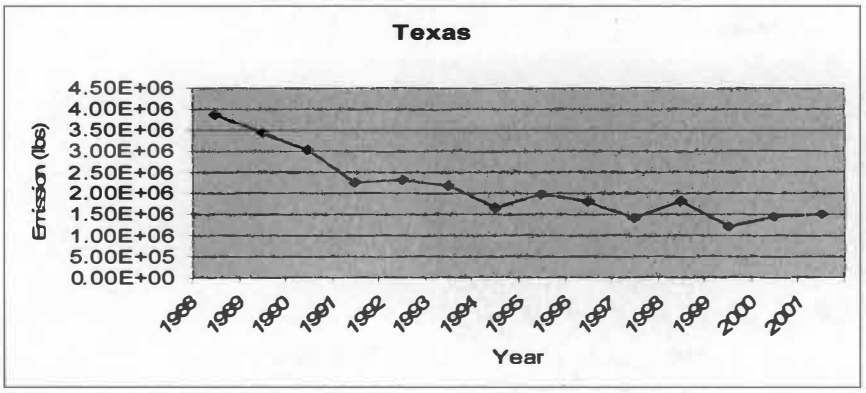


c)

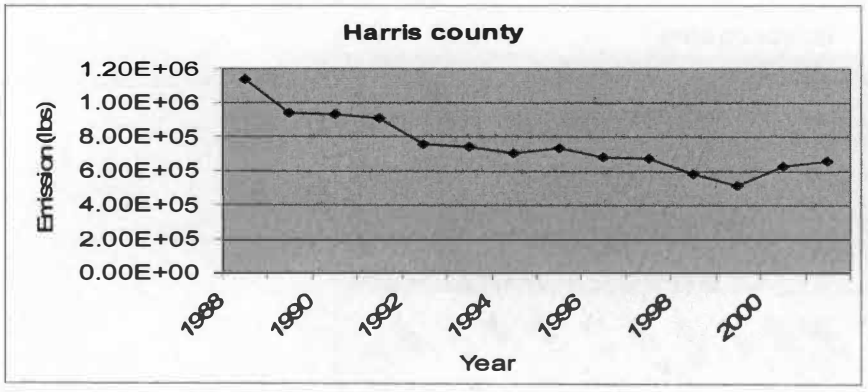
Figure 10 Benzene emissions trend from Toxic Release Inventory. a) USA b) Texas c) Harris County



a)

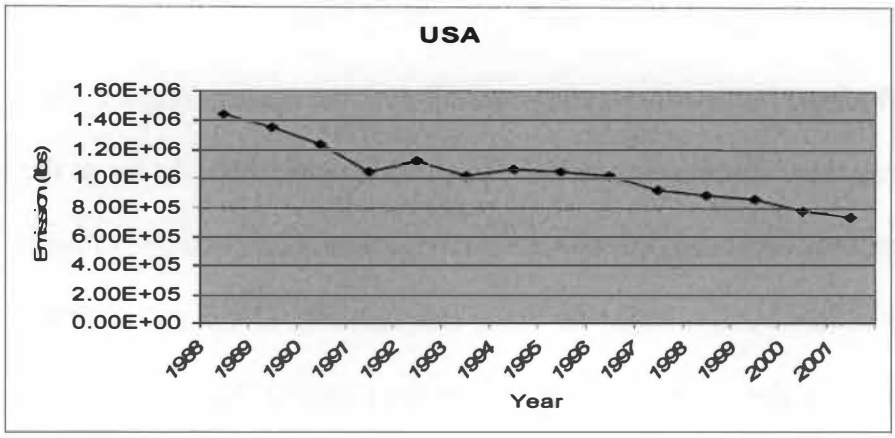


b)

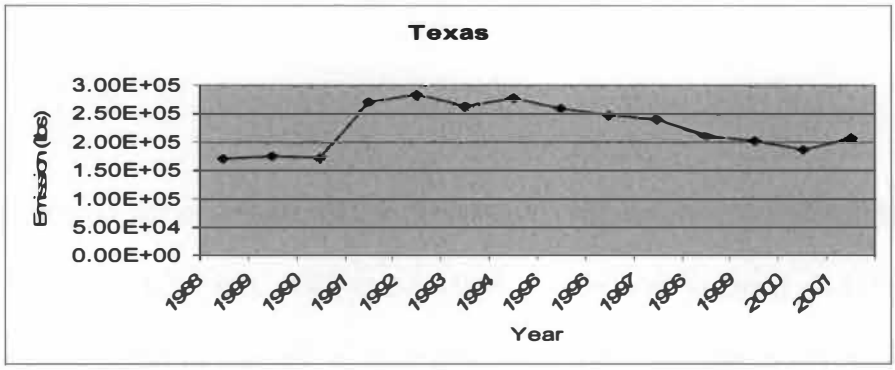


c)

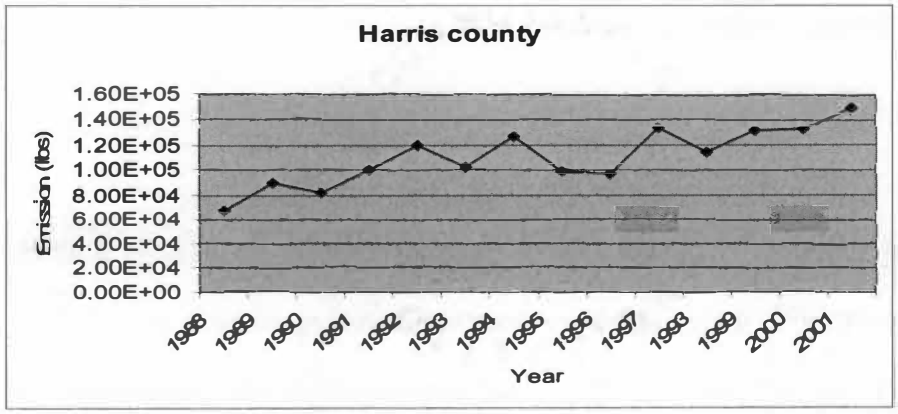
Figure 11 1, 3 Butadiene emissions trend from Toxic Release Inventory. a) USA b) Texas c) Harris County



a)



b)



c)

Figure 12 Vinyl chloride emissions trend from Toxic Release Inventory. a) USA b) Texas c) Harris County

Trichloroethylene

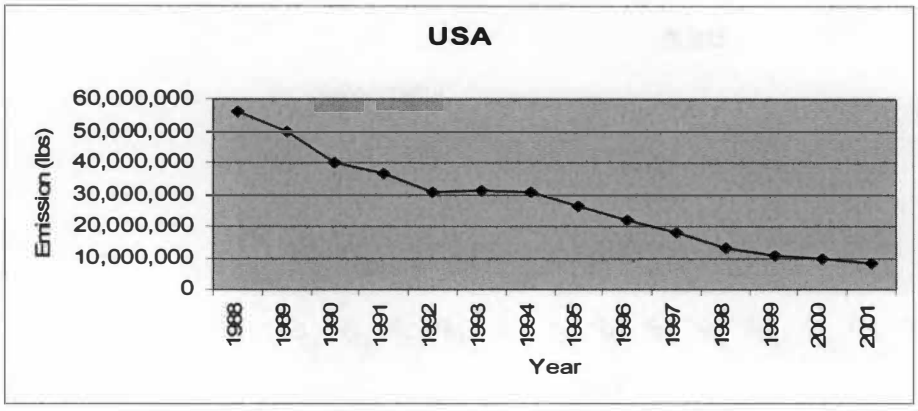
A steady decrease is observed in the case of emissions all over the country (Figure 13a). Emissions in the country were constant between the years 1992 and 1994. As far as the state of Texas (Figure 13b) is concerned emissions have consistently decreased for almost all the years. An inconsistent trend is observed in the Harris county (Figure 13c), in the year 1996 the emissions in the county rose by a factor of approximately 10. This inconsistency may be a result of a reporting error, given the large shift in 1990 and 1996 emissions.

Perchloroethylene

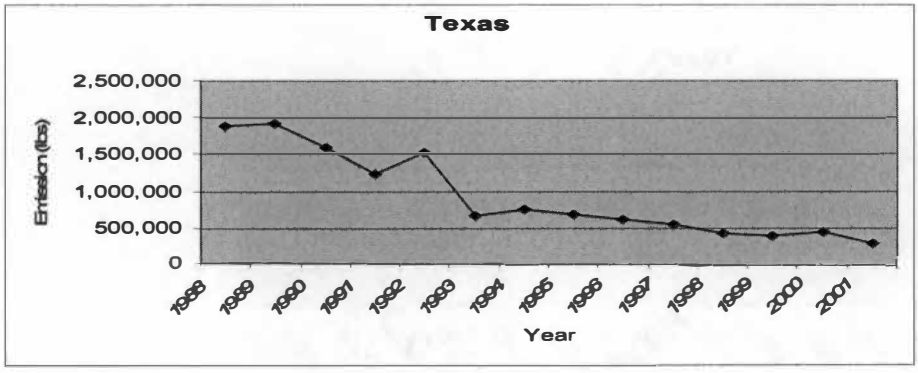
A steady decrease in emissions is observed in the case of total emissions in the country (Figure 14a). Despite of an increase in emission in the years 1991 and 1994 the total emissions in the state of Texas (Figure 14b) have decreased in the last thirteen years. Harris county emissions (Figure 14c) have decreased significantly, particularly during the year 1990 when a steep fall in emission was observed.

Dichloromethane

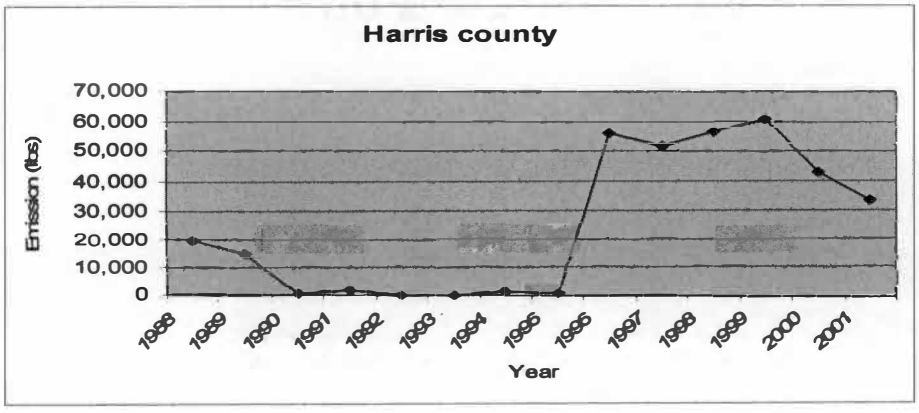
Emissions in the country (Figure 15a) have steadily decreased. As far as the state (Figure 15b) is concerned, except 1993, there has been a decrease in emissions each year. In the case of Harris County (Figure 15c) after a steep initial increase emissions have followed a decreasing trend. County emissions were nearly consistent between the years 1995 and 1998.



a)

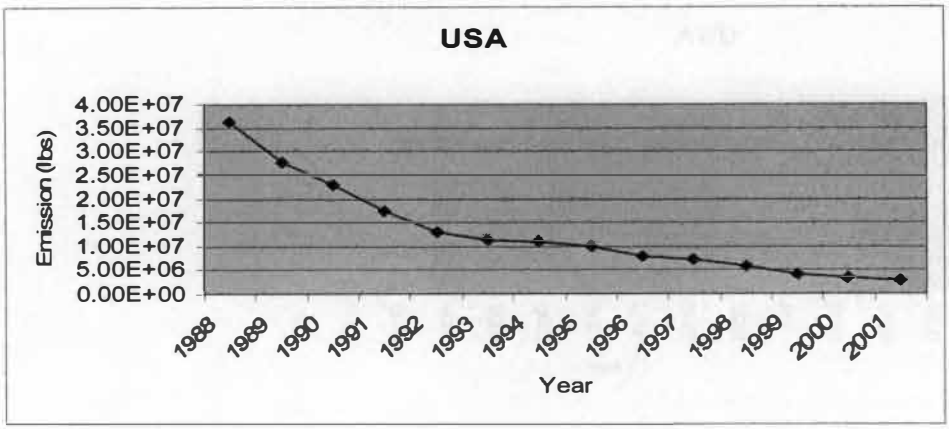


b)

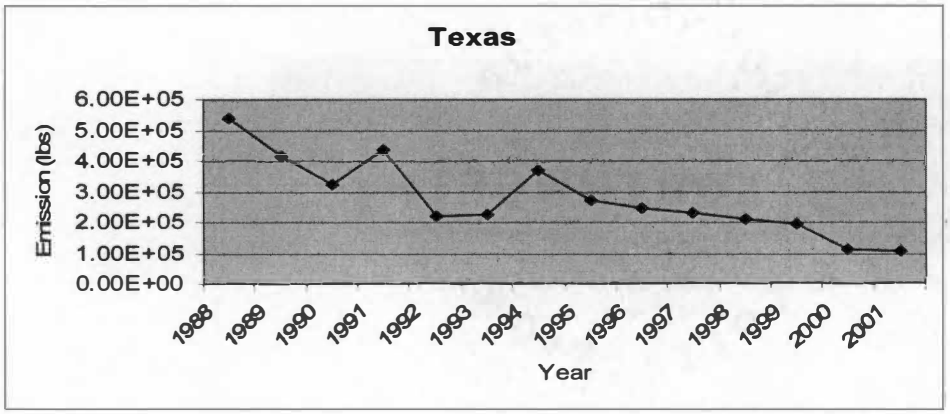


c)

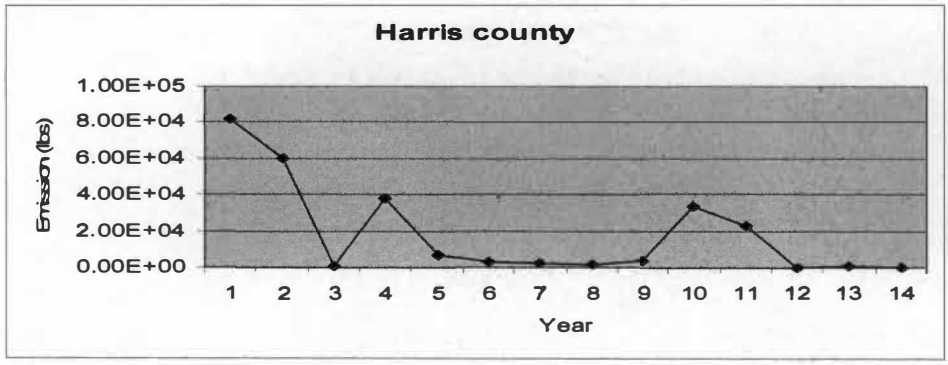
Figure 13 Trichloroethylene emissions trend from Toxic Release Inventory. a) USA b) Texas c) Harris County



a)

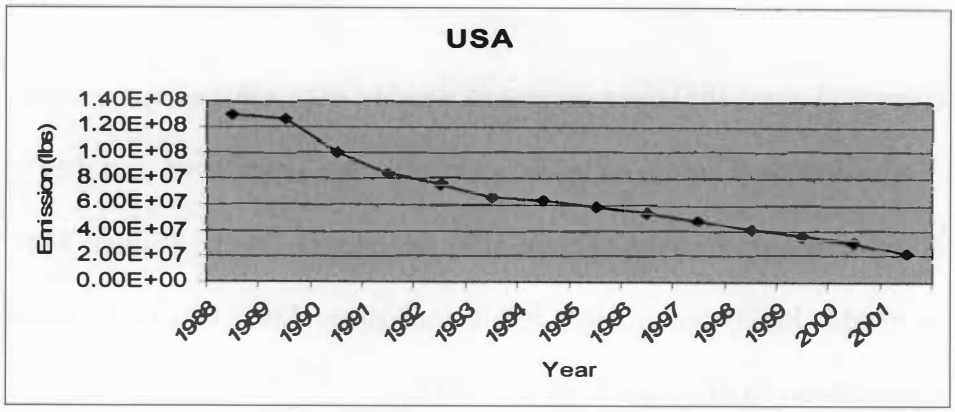


b)

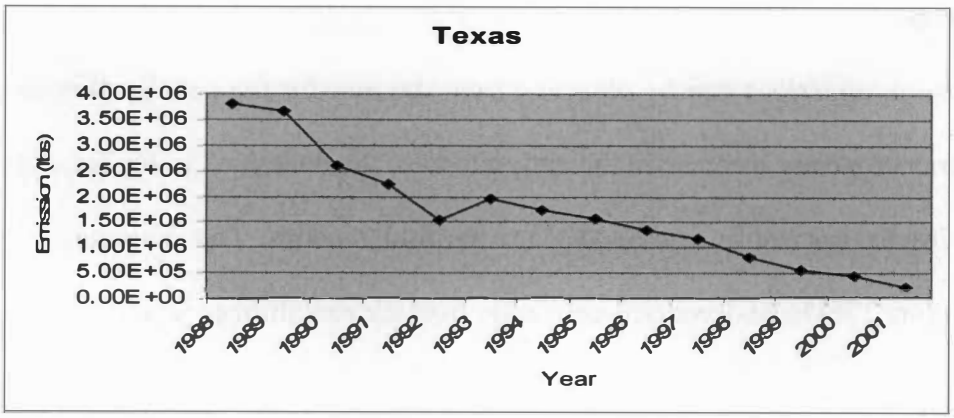


c)

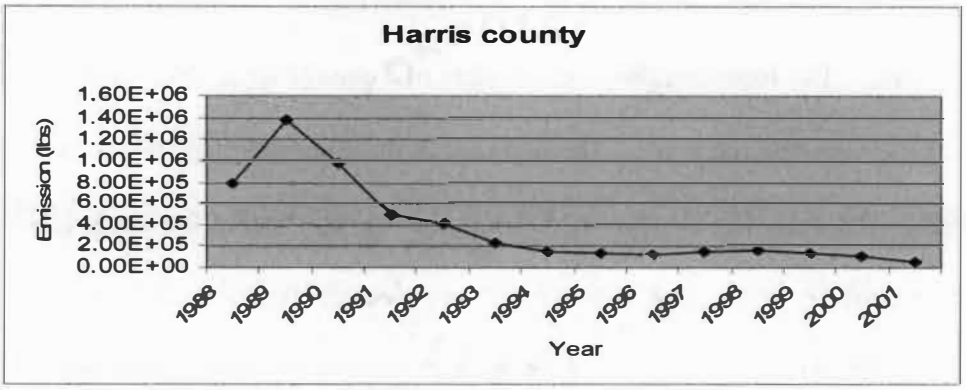
Figure 14 Perchloroethylene emissions trend from Toxic Release Inventory. a) USA b) Texas c) Harris County



a)



b)



c)

Figure 15 Dichloromethane emissions trend from Toxic Release Inventory. a) USA b) Texas c) Harris County

Ethylene oxide

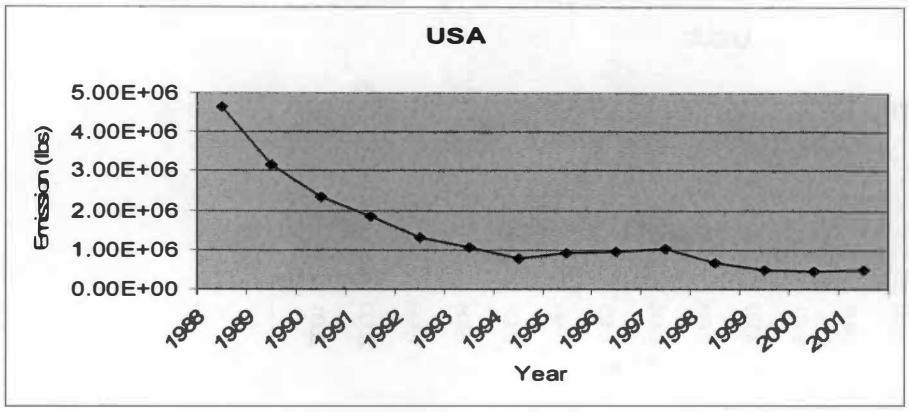
Emissions in the country (Figure 16a) have decreased steadily except between the years 1995 and 1997. Emissions were nearly consistent between the years 1995 and 1997. Though the overall emissions in the state (Figure 16b) and Harris County (Figure 16c) have decreased, the trend is highly inconsistent and inconclusive. Emissions in the state were highly inconsistent between the years 1989 and 1993.

Ethylene dichloride

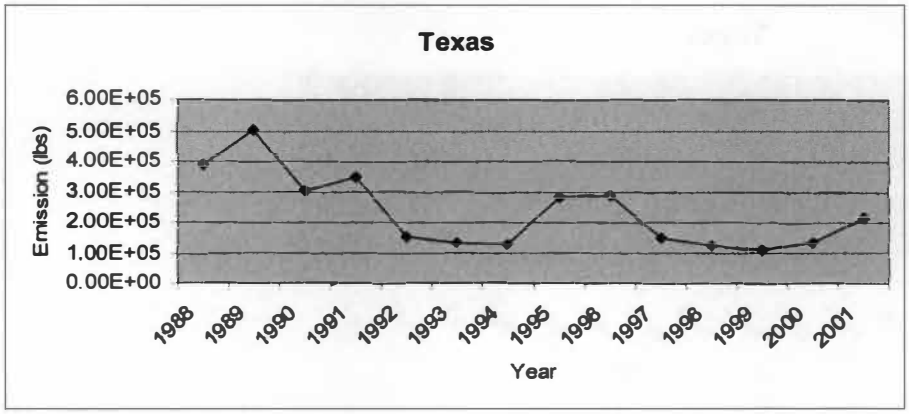
A smooth decrease in emissions can be observed from the plot for the country (Figure 17a). After experience steady increase in the early nineties, the emissions in the state of Texas (Figure 17b) have steadily decreased from the mid nineties. The emissions in Harris County (Figure 17c) have decreased unsteadily over the past thirteen years.

Ethylene dibromide

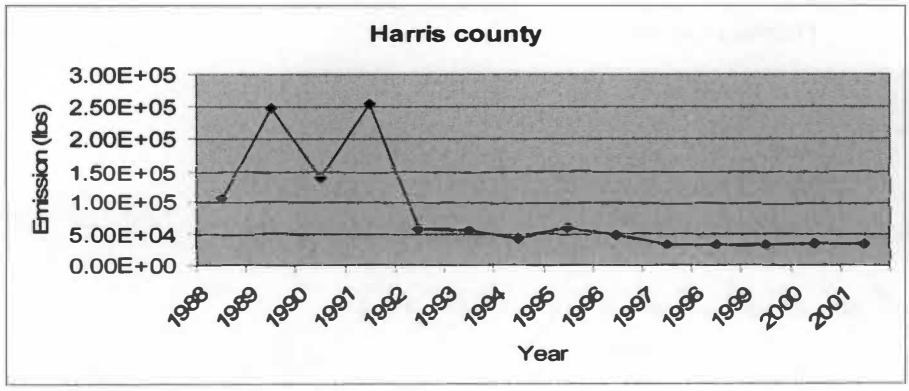
After an initial increase the overall emissions in the country (Figure 18a) have decreased over the last few years. The total emissions in the state of Texas (Figure 18b) have been steadily increasing over the last ten years. The increase in the state was significant in the year 1992 and 1995. The emission trend was highly inconsistent between the years 1991 and 1996. Total emissions in the last nine years have decreased; no emissions were reported in the year 1992 (Figure 18c). A decreasing trend can be observed in the last three recorded years.



a)

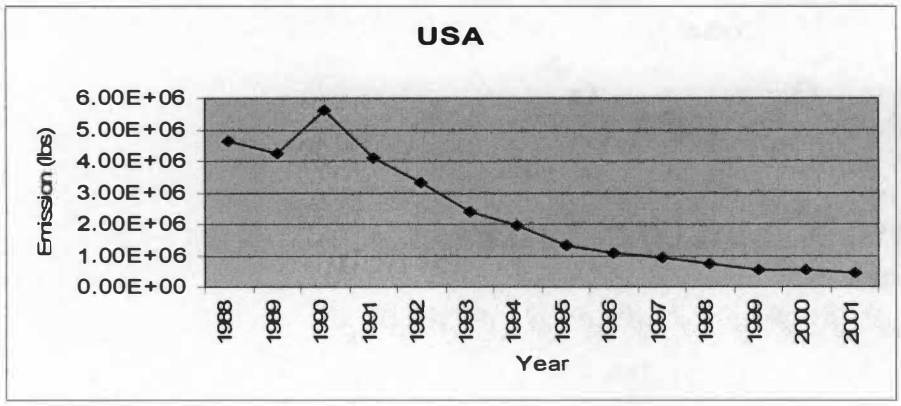


b)

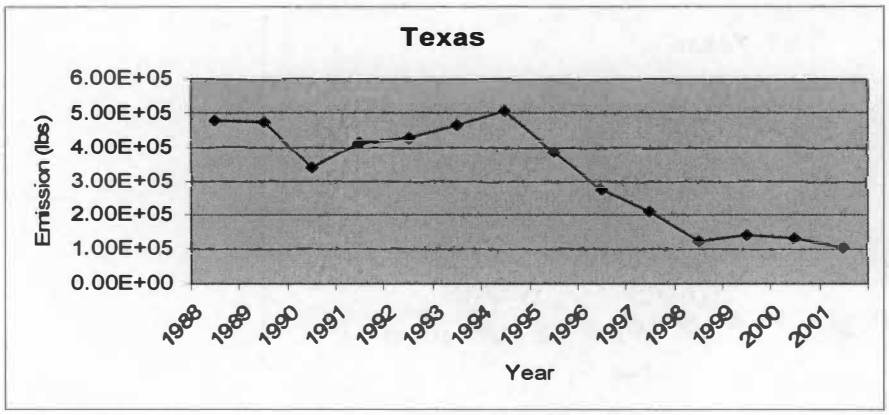


c)

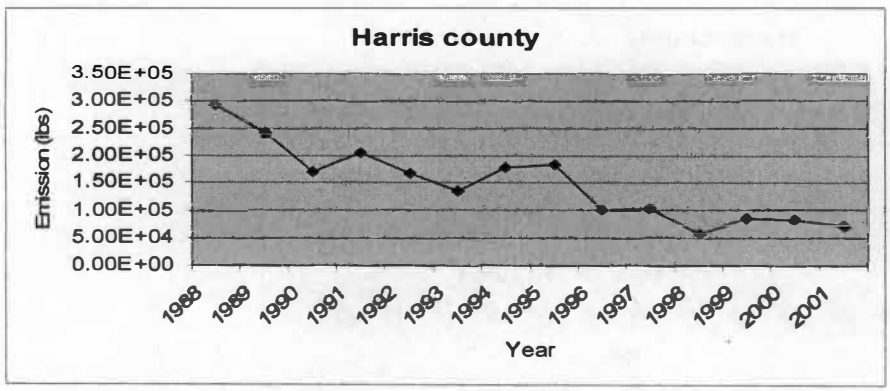
Figure 16 Ethylene oxide emissions trend from Toxic Release Inventory. a) USA b) Texas c) Harris County



a)

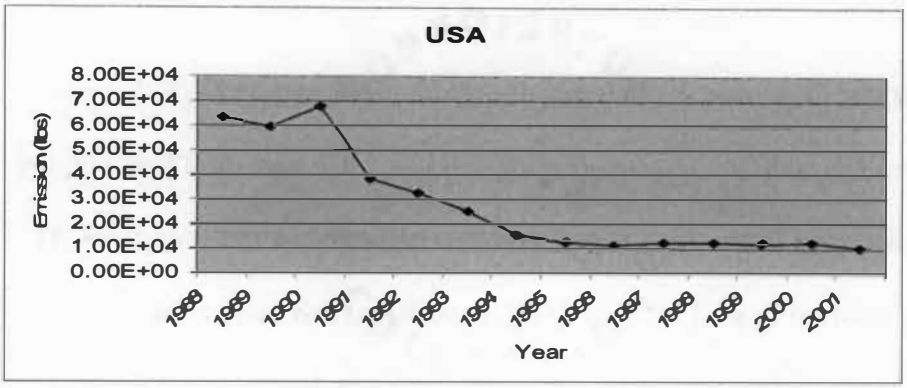


b)

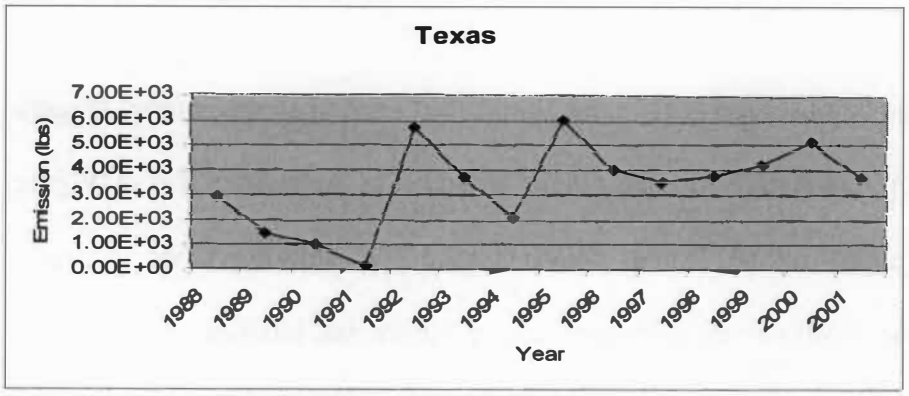


c)

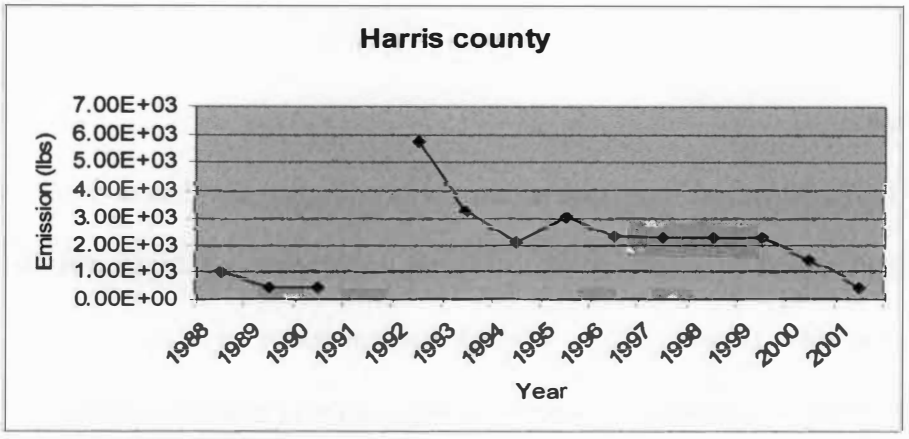
Figure 17 Ethylene dichloride emissions trend from Toxic Release Inventory. a) USA b) Texas c) Harris County



a)



b)



c)

Figure 18 Ethylene dibromide emissions trend from Toxic Release Inventory. a) USA b) Texas c) Harris County

Dichloropropane

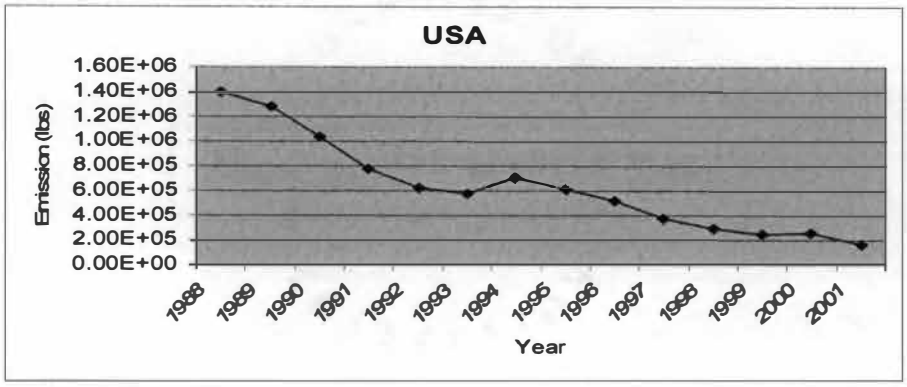
Despite of slight increase in emissions between the years 1993 and 1994, a decreasing trend can be observed for both the country (Figure 19a) and the state of Texas (Figure 19b). A significant decrease in the state's emission was observed in the year 1989. The emissions in Harris County (Figure 19c) are highly inconsistent and inconclusive. Harris County emission trend was highly inconsistent between the years 1991 and 1997.

Chloroform

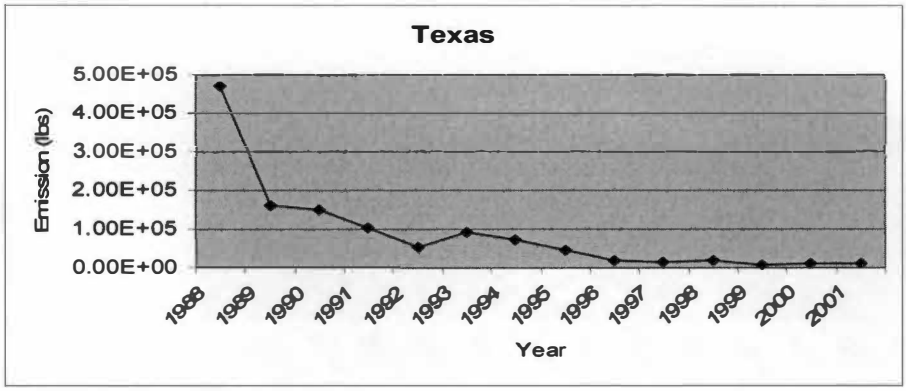
A steady decrease can be observed in the total chloroform emitted in the country (Figure 20a). Despite some initial fluctuation, the overall emission in the state of Texas (Figure 20b) has decreased significantly. Harris county (Figure 20c) emission trend is almost similar to that of Texas, with a sharp decrease occurring in the late nineties. A significant increase in emissions was observed in the year 1992 and significant decrease in emission was observed in 1997.

Carbon Tetrachloride

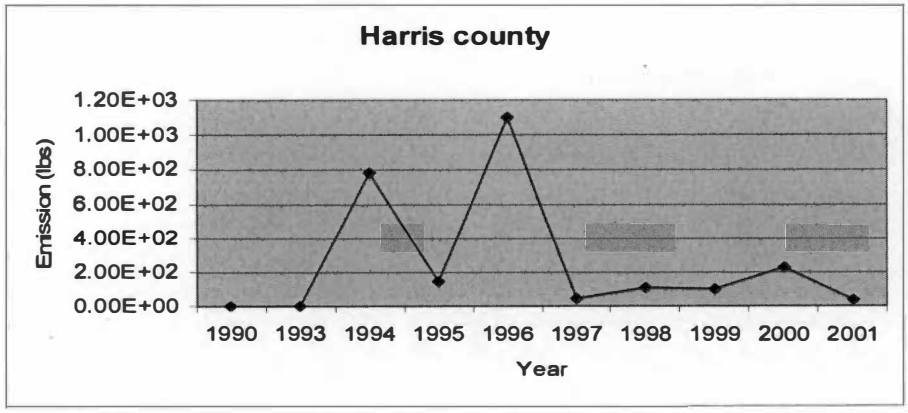
Apart from the year 1993, the overall emission in the country (Figure 21a) has decreased significantly. After an initial increase, an inconsistent but decreasing trend can be observed for the Texas state (Figure 21b). Though the emissions in Harris County (Figure 21c) have constantly decreased, an increase in emission was recorded in the year 2001.



a)

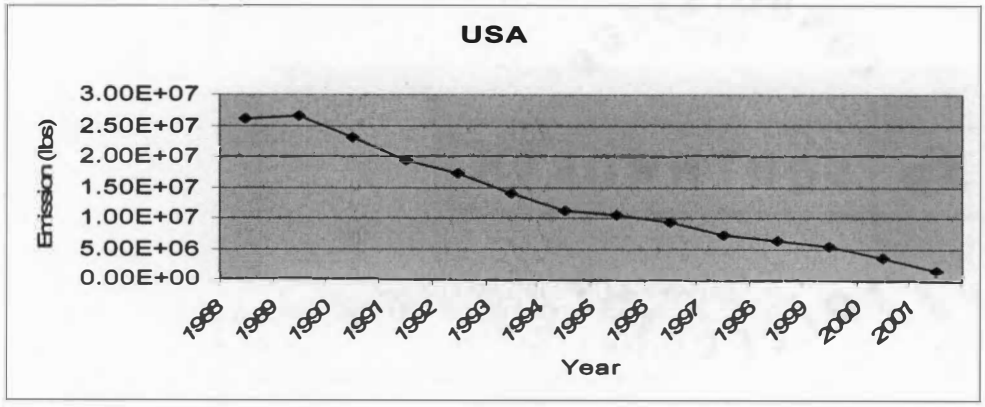


b)

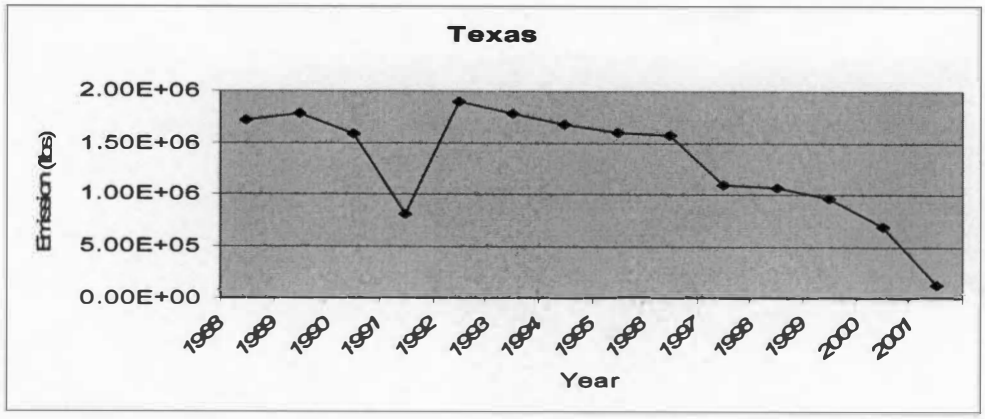


c)

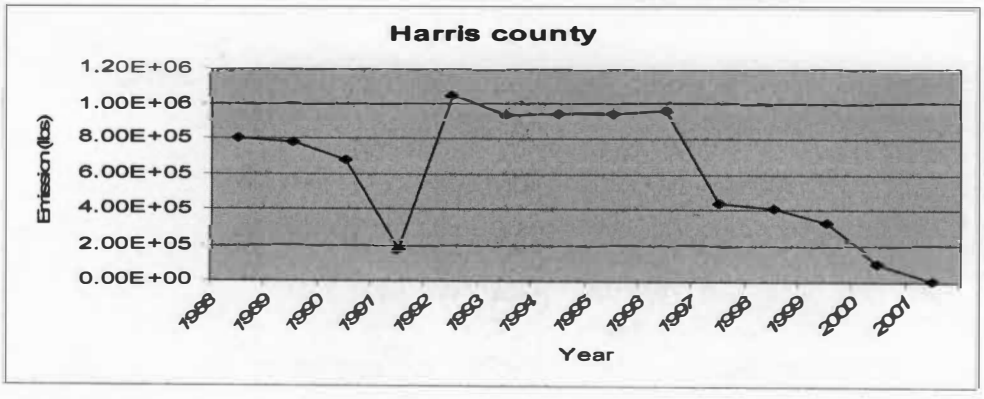
Figure 19 Dichloropropane emissions trend from Toxic Release Inventory. a) USA b) Texas c) Harris County



a)

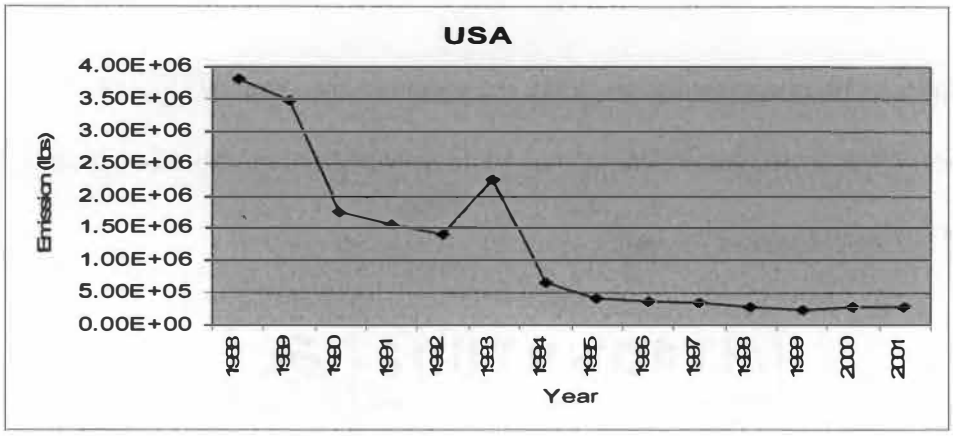


b)

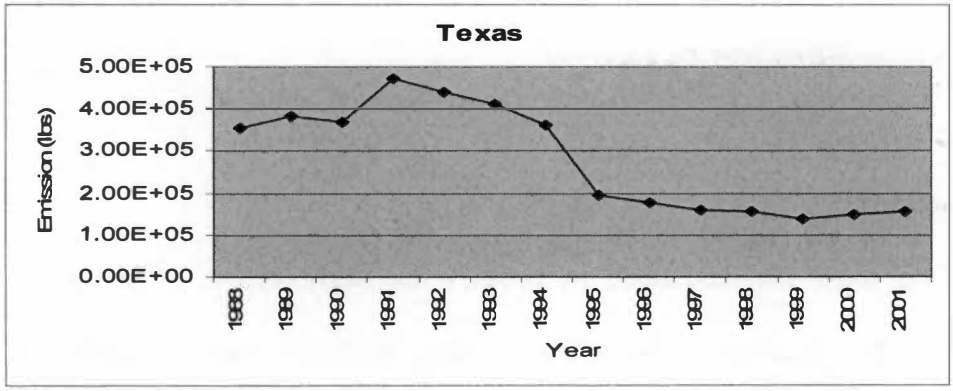


c)

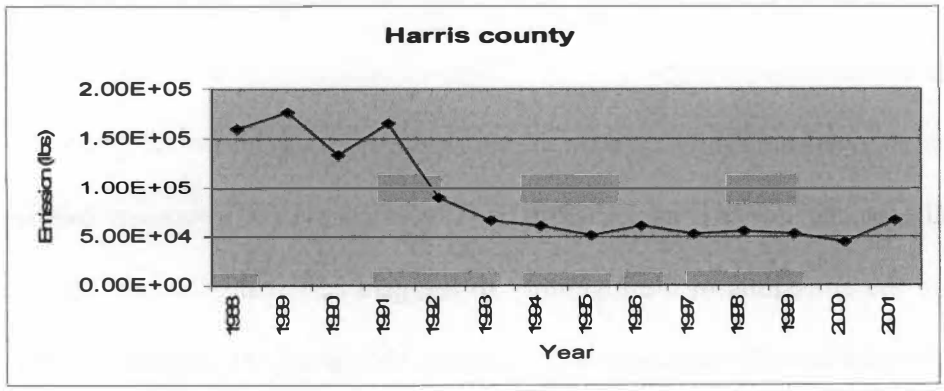
Figure 20 Chloroform emissions trend from Toxic Release Inventory. a) USA b) Texas c) Harris County



a)



b)



c)

Figure 21 Carbon Tetrachloride trend from Toxic Release Inventory. a) USA b) Texas c) Harris County

Acetaldehyde

An increasing trend can be observed for the total emissions in the country (Figure 22a), while an inconsistent but a decreasing trend can be observed for both the Texas state (Figure 22b) and Harris county (Figure 22c).

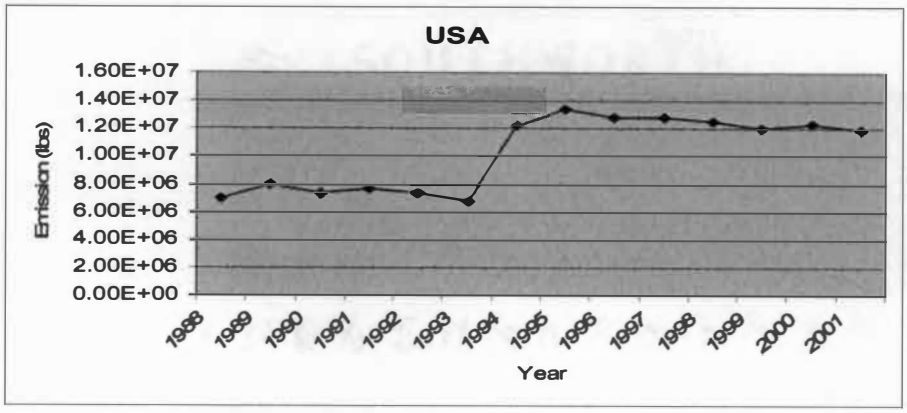
Acrylonitrile

Almost a steady decrease can be observed in the emission trend for the nation (Figure 23a). In the case of the Texas state (Figure 23b) and Harris County (Figure 23c) a fluctuating, but decreasing trend can be observed.

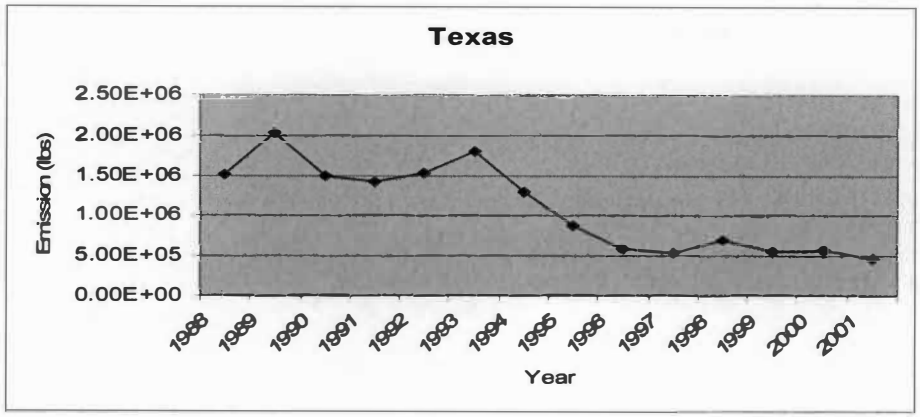
2.2 Emission Processor

Emission processing tools are developed to convert the fairly coarse geographical coverage found in the inventory database to a finer grid-cell scale required by photochemical models (Hogrefe, 2003). Normally emission inventories for different pollutants are compiled at the county level, for an average summer day or average annual day (Hogrefe, 2003).

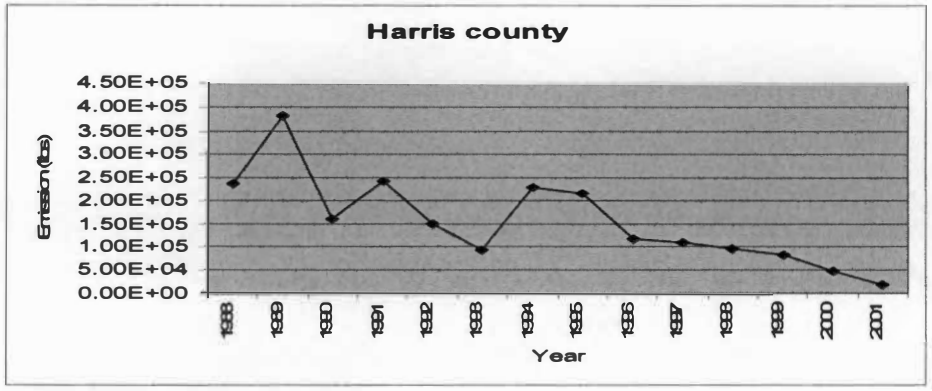
The air quality models need emissions data on an hourly basis, for each model grid cell, and for each model species (SMOKE manual, 2003). The function of a processing tool is to spatially allocate the emissions in the inventory to the grid cell scale selected by the user, resolve emissions temporally and chemically speciate the pollutants according to the selected chemical mechanism (Hogrefe, 2003).



a)

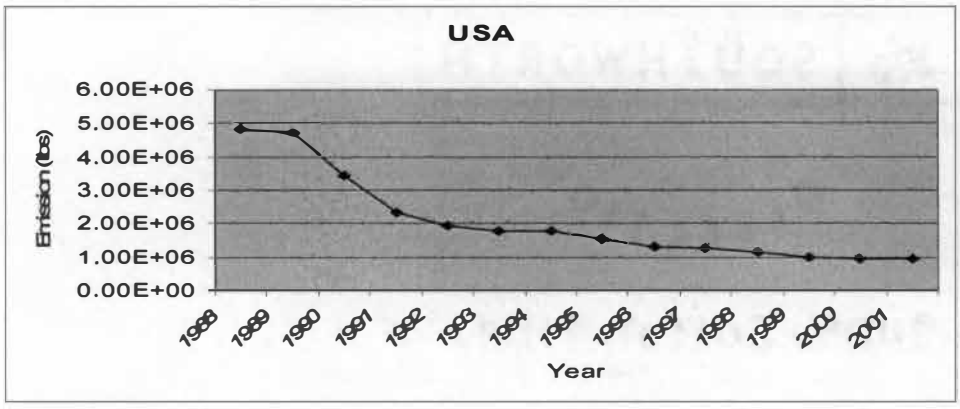


b)

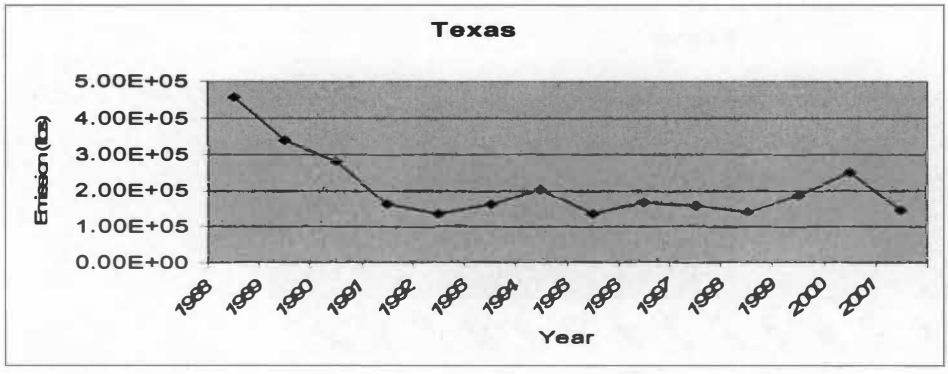


c)

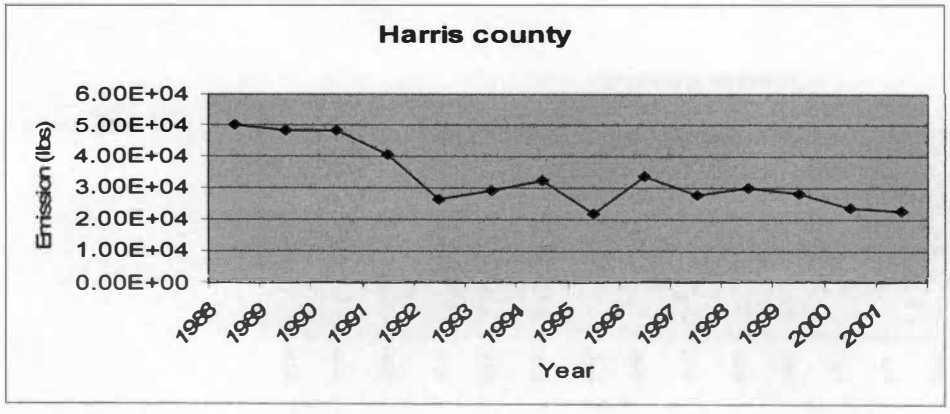
Figure 22 Acetaldehyde emissions trend from Toxic Release Inventory. a) USA b) Texas c) Harris County



a)



b)



c)

Figure 23 Acrylonitrile emissions trend from Toxic Release Inventory. a) USA b) Texas c) Harris County

2.2.1 Types of Emission processing tools

At present the various emission processing tools which are used for regional and urban-scale air quality modeling are Emission Modeling System -2001 (EMS-2001), Emissions Preprocessor System – Version 2.5 (EPS2.5), and the Sparse Matrix Operator Kernel Emissions (SMOKE) model. These models are used in both research and regulatory applications (Hogrefe, 2003).

EMS-2001

The EMS-2001, originally called Geocoded Emission Modeling and Projection system (GEMAP), was developed in the late 1980s by Radian Corporation. In mid-1990s the tool was significantly modified and was subsequently renamed as EMS-95. The system, which is written in SAS, has undergone several updates and modification since the mid-1990s and is currently named as EMS-2001. The three key components of this system are area, point, and mobile source emissions modules. The point and area source modules convert annual emissions to gridded, speciated, hourly emission estimates based upon the source type. The mobile source module estimates gridded hourly emissions corrected for temperature, based on traffic (VMT) and vehicle mix data. To generate speed and temperature adjustments and also to develop emission factors this model incorporates EPA's MOBILE5b model in its processing. The EMS-2001 tool can be used on several different computer platforms and it also has the ability to support different chemical speciation schemes (Hogrefe, 2003). To process toxic air pollutants a separate emission processing tool called Emission Modeling System for Hazardous Air Pollutants (EMS-HAP) is used (SCRAM, user guide, 2002).

EPS 2.5

Emission Preprocessor System is defined as a system of computer programs, which adjusts a county-level emissions inventory for input to an air quality model like Urban Airshed Model. EPS 2.5 is an emission processing tool recommended by the EPA's office of Air Quality Planning and Standards for State Implementation Plan (SIP) modeling demonstrations. The system contains a series of FORTRAN modules that execute the intensive data manipulations required to integrate spatial, temporal, and chemical resolution into an emissions inventory used for photochemical modeling. The SAS interface present in the system provides a user friendly processing environment for EPS setup, quality control and graphics activities (SCRAM001, uamz6 1992).

SMOKE

The MCNC Environmental Modeling Center (EMC) developed Sparse Matrix Operator Kernel Emissions (SMOKE) modeling system to combine emissions data processing method to high performance computing (HPC) sparse-matrix algorithms. The SMOKE system is an important addition to the existing resources for decision making about emission controls for both urban and regional applications. It offers a mechanism for preparing specialized inputs for air quality modeling research, and it makes air quality forecasting feasible. The main features of this tool are its ability to process emissions with user-selected chemical mechanisms and emissions processing for reactivity assessments. The tool has the ability to process both criteria and toxic pollutants emissions (SMOKE manual, 2003). The SMOKE processing tool was created based on an early recognition that the matrix computation paradigm in a Fortran program for

modeling point, mobile, area, and biogenic emissions, is much quicker than earlier sequential processing programs, i.e., one type of operation at a time, that rely on SAS software (Benjey, 2002).

2.2.2 SMOKE version 2.0

The emission processing tool used in this thesis was "SMOKE version 2.0". The version was released in September 2003 and it has the ability to process both criteria and toxic pollutants released by all the four types of sources (point, area, mobile and non-road) with user selected mechanism. Prior to SMOKE the general layout of atmospheric emissions models was a network of pipes and filters. In these models, at any given step in the processing an emissions file included self contained records describing each source and all of the characteristics acquired from previous processing stages. Every processing stage acted as a filter that inputs a stream of these fully – defined records, integrates it with data from one or more ancillary files, and generates a new stream of these records. During this process surplus data were passed down the pipe at the cost of extra input/output storage, data processing, and program complexity. This process worked well in old computers, which had very small available memories and tape-only storage, but was not suitable for current desktop machines or high-performance computers. The difference in speed was observed when the Emission Preprocessor System (EPS) 2.0 was run on a Cray Y-MP (a fast computer). The EPS 2.0 processor ran four times slower on the Cray machine than on a desktop 150MHZ DEC Alphastation 3000/300. The main cause for the slow performance is the serial approach followed by the model. Most of the models used prior to SMOKE followed a series approach shown. A detail study was

conducted and it was discovered that emissions computation would be more adaptable to high performance computing if the pattern followed were appropriately changed (Figure 24). A new emission processing tool called SMOKE was developed with a pattern more adaptable to high speed computers. SMOKE emission processing tool operates under the concept called sparse matrix operations.

In this inventory emissions are organized as a vector of emissions sorted in a particular order, with associated vectors that include characteristics about the sources such as the state/county and SCCs. The system then creates matrices that apply the gridding, speciation, and temporal factors to the vector of emissions. These matrices are mostly independent from one another, and can therefore be generated in parallel (Figure 25) and applied to the inventory in a final merge step, which integrates the inventory emissions vector with the control, speciation, and gridding matrices to create model-ready emissions.

SMOKE version 2.0 is primarily an emissions processing system and is not an emission inventory preparation system. Its main function is to provide an efficient tool for converting emission inventory data into the formatted emissions input files required by an air quality model. The tool supports Inventory Data Analyzer (IDA) formats, Emission Modeling System' 95 (EMS-95) format, and a SMOKE one-record-per-line format.

The records in the National Emission Inventory (NEI) can be readily converted to the IDA formats or One Record per Line (ORL) format (SMOKE manual 2003). The various steps in the processing are described as follows

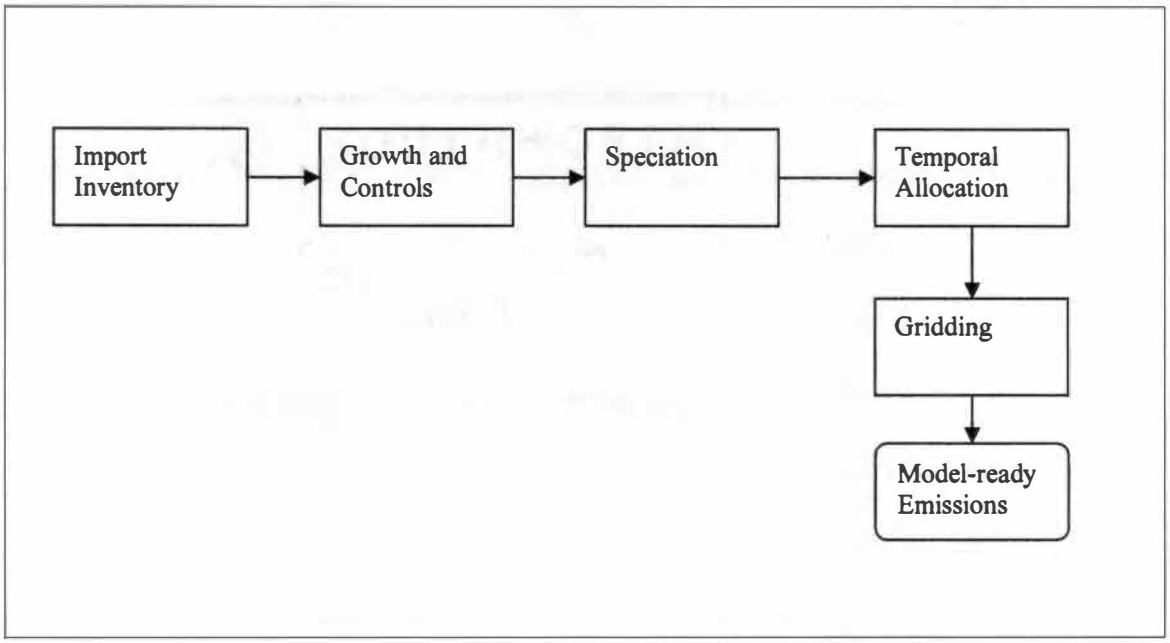


Figure 24 Serial approach to emission processing

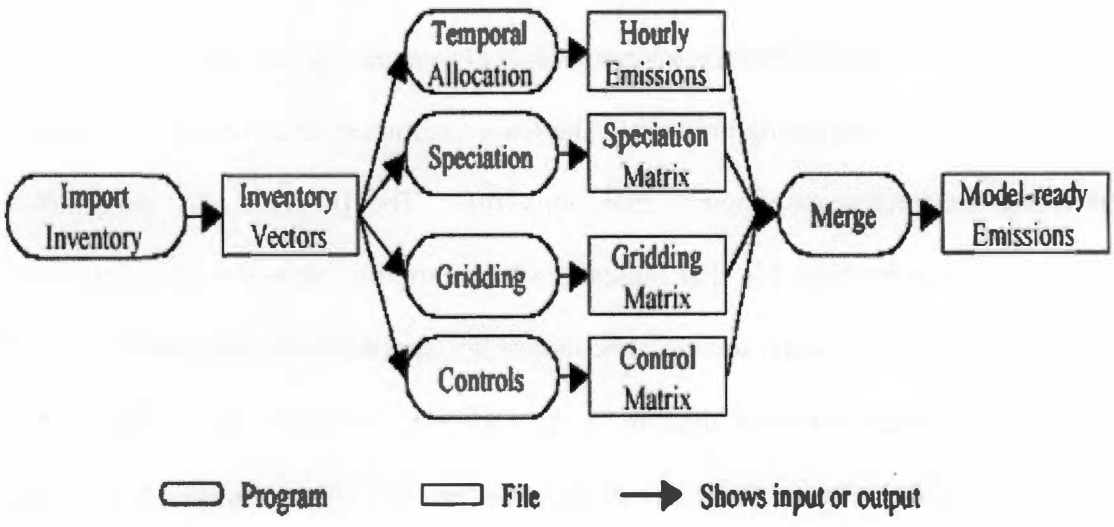


Figure 25 Parallel approach followed by SMOKE (manual)

Inventory import

The importing of emission inventory and related data is the first processing step needed for any emissions processing tool. The "Smkinven" program in the model performs this task. The functions of this program are to check the formats of the input files, assign pollutant names by code numbers, select pollutants from the input files, combine all annual and / or average-day data into a consistent inventory, combine toxics and criteria inventories, eliminate duplicate mass using either an integrate or non-integrate approach, sort the inventory records into the order expected by other SMOKE programs, aggregate or disaggregate toxics emissions data as specified by user inputs, assign point source locations to area sources, convert units of emissions and activities to the units used in the SMOKE intermediate inventory, set weekdays averaging approach, assign county codes, years, and time zones, report results of import including pollutant totals for toxics data and other information needed for quality assurance (SMOKE manual 2003).

Temporal processing

The temporal allocation of emission inventory data always occurs upon the completion of the inventory import processing program. The main function of the "Temporal" program is to create an intermediate hourly emissions file. The program also generates a supplementary intermediate file that indicates which monthly, day-of-week, and hourly profiles were assigned to each source. The factors are applied on the basis of the source characteristics in the emissions data from the SMOKE inventory files. The factors include monthly, day-of-week, and hourly temporal profiles. The resulting data vectors have hourly emissions for the inventory species. Almost all the calculations are

implemented as sparse-matrix algebra based upon temporal cross-references and sets. In the case of mobile sources, hourly emissions values depend on meteorology (SMOKE manual 2003).

Chemical Speciation processing

The model chemical mechanism contains a simplified set of equations that utilize "model species" to represent atmospheric chemistry. The emission processor requires the speciation profiles to convert the emissions in terms of pollutant values to the species used in the photochemical mechanism. The function of the chemical speciation processing program Spcmat is to produce matrices that contain the factors for converting the input emissions pollutants to the model species used in the air quality models. The speciation matrices generated by Spcmat are used to transform column vectors of inventory-pollutant emissions into column vectors of model-species emissions. The major functions of the Spcmat program are to split inventory pollutants into chemical species, make pollutant-to-pollutant conversions, check the consistency of the speciation profiles with the inventory table, set the order of the output species and to create speciation output files (SMOKE manual 2003).

Spatial processing

The spatial processing operation, or gridding, integrates the grid specification for the air-quality modeling domain with source locations from the SMOKE inventory file. The gridding matrix formed is a sparse matrix that describes in which grid cells the emissions for each source occur within the modeling domain. The gridding matrix is applied to the

inventory emissions to convert source-based inventory emissions to gridded emissions. The SMOKE "Grdmat" program develops the gridding matrix for area, mobile, and point sources. The gridding method is different depending on the type of source being processed. In the case of area sources, county-total emissions are spread among the cells intersecting the county through the use of gridding surrogates. For mobile sources, the data can be generated by county or as line sources. County-based mobile emissions are apportioned with gridding surrogates, normally with surrogates based on the different road types for which the mobile emissions are provided. The line source emissions are apportioned depending on the length of the links in each cell. In the case of point sources, emissions are apportioned to the grid cell intersecting the point source. The gridding matrix has the SMOKE source IDs that intersect each grid cell and the source to cell factors for each (SMOKE manual 2003).

Control Processing

The control processing operation applies control factors from a control input file based on source characteristics in the inventory. The control scenario definition has instructions on how to change the values of emissions based on regulations affecting industrial activities or personal behavior. The control matrix is created by the "Cntlmat" program of SMOKE. The matrix depends only upon the source characteristics in the SMOKE inventory and the set of controls chosen. The Cntlmat program performs control processing for SMOKE area, mobile, and point sources; however, much more complex controls for on-road mobile sources can also be implemented when using MOBILE6 through SMOKE to calculate emission factors and apply them to VMT. The emission

control factors can be applied in addition to the emissions growth factors, and the net effect of this growth and control is called "projection". SMOKE control processing can create two types of control matrices during a given run: a multiplicative control matrix and a reactivity control matrix. The main tasks of Cntlmat program are assigning control factors from six control packets to the sources, reporting on factors assigned to each source in the inventory, creating multiplicative control matrix, and creating reactivity control matrix (SMOKE manual 2003).

Merging

Generating emissions with SMOKE that are ready for input to an air quality model should always include merging the hourly emissions created during temporal processing with the gridding matrices and the speciation matrices. In the case of point sources for CMAQ or MAQSIP, developing the model ready emissions must also include creating the ASCII elevated file. The function of Smkmerge program is to perform these processing steps using vector-matrix multiplication to integrate the matrices and layer fractions with the hourly emissions vectors from the temporal program. In the case where the overall SMOKE processing setup includes running the nonroad mobile category as separate runs, Smkmerge cannot be used to combine all source categories in to single output file. In such a situation the Mrggrid program combines the model ready files from individual source categories (i.e.) from separate SMOKE runs for stationary area, non road mobile, windblown dust, on-road mobile and point sources. The number of model ready files, which can be combined by Mrggrid into a single model ready file, is not limited. Smkmerge program also has the capability to input hourly emissions by day

of the week and reuse days that are the same. Though SMOKE processor generally follows the parallel sequence approach shown, there are some exemptions when it comes to individual source categories.

Area source processing

The area source processing of SMOKE is done in two major ways; one is called the typical route and the other pregridded data route.

a) Typical route: The typical route (Figure 26) or the normal route involves processing data identified by country/state/county codes and SCCs. A layout of the sequence followed by this program is shown below. The inventory import step reads the input emissions data, screens, processes them, and converts the raw data to the SMOKE intermediate inventory file. During the temporal allocation process the file are subdivided to hourly emissions. Chemical speciation factors and spatially allocation factors are assigned during the speciation and gridding

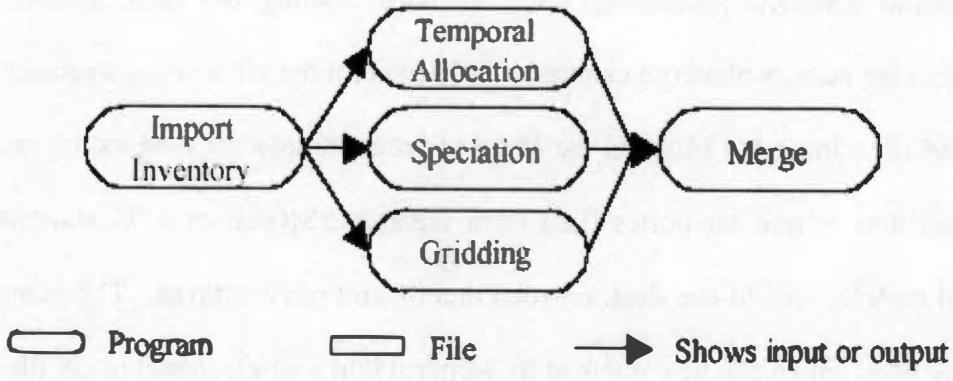


Figure 26 Area source processing layout (SMOKE manual, 2003)

process respectively. The merge step combines all the intermediate files to create model ready emissions.

b) Pregridded data route

The second method for area source processing involves the use of pregridded data. The approach requires the inventory emissions data to be gridded prior to inventory import. Though the gridding step is quite trivial when the grid cell numbers are already specified the gridding step must still be run to generate gridding matrix required for the merge step (SMOKE manual 2003).

Biogenic source processing

A layout of biogenic –source processing steps and intermediate files is shown in the Figure 27. The raw land use inventory data are converted to normalized emissions by the processor. The normalized emissions are then subjected to meteorological adjustments in order to create hourly model-ready emissions estimates (SMOKE manual 2003).

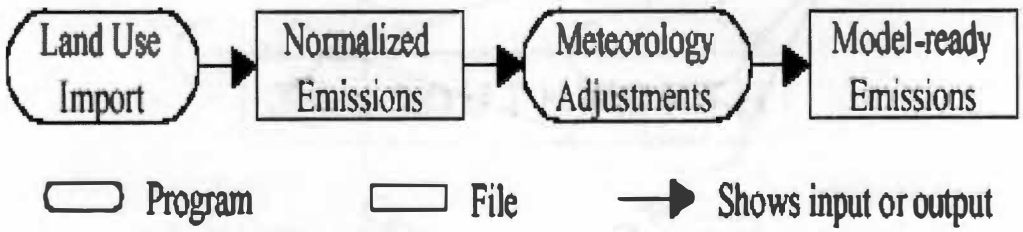


Figure 27 Biogenic source processing (SMOKE manual 2003)

Point-source processing

Point source emission processor converts annual, daily, or hourly emissions to hourly and gridded model-ready emissions of the chemical species used by an air quality model. The general layout of point source processing is shown in Figure 28. The inventory import step reads the raw emissions data, screens, process them, and converts the data to the SMOKE intermediate inventory file. The inventory file emissions are subdivided to hourly emissions during temporal allocation; assigned chemical speciation factors and spatial allocation factors during speciation and gridding stages respectively. The plume-rise computation predicts vertical plume rise of emissions sources and computes the fraction of emissions from the sources to go in to the model layer. The results of these steps are merged in the merge step, which creates model ready files (SMOKE manual 2003).

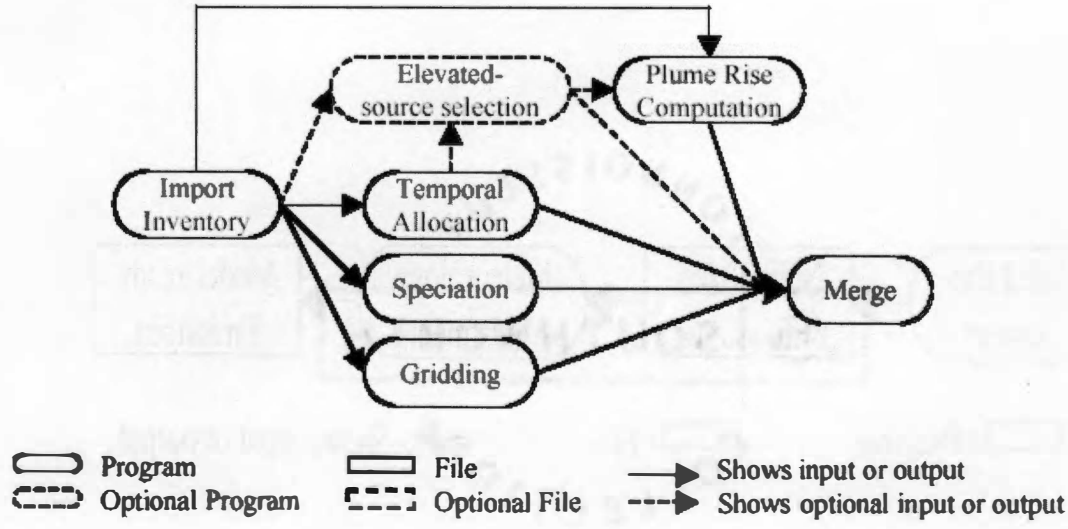


Figure 28 Point source processing (SMOKE manual, 2003)

Mobile-source processing

Mobile source emissions can be processed with SMOKE in two different ways. The first method is to compute mobile emissions values prior to running SMOKE and provide it to SMOKE as input; this method is called precomputed emissions approach.

The second method is to provide SMOKE with VMT data, meteorology data, and MOBILE 6 inputs and have SMOKE compute the mobile emissions based on these data; this approach is called VMT approach. The basic layout of mobile source processing is shown in Figure 29. The precomputed emissions approach is similar to that of area source processing. The VMT approach is different from the first approach mentioned. The VMT data by road class and vehicle type are given as input to SMOKE. MOBILE6 preprocessing is done on the standard MOBILE 6.2 input files to provide input to SMOKE's driver for MOBILE 6.2. The gridding step allocates the link sources to the grid cells and utilizes spatial surrogates to allocate county-total emissions to grid-cells, storing the factors needed for this allocation.

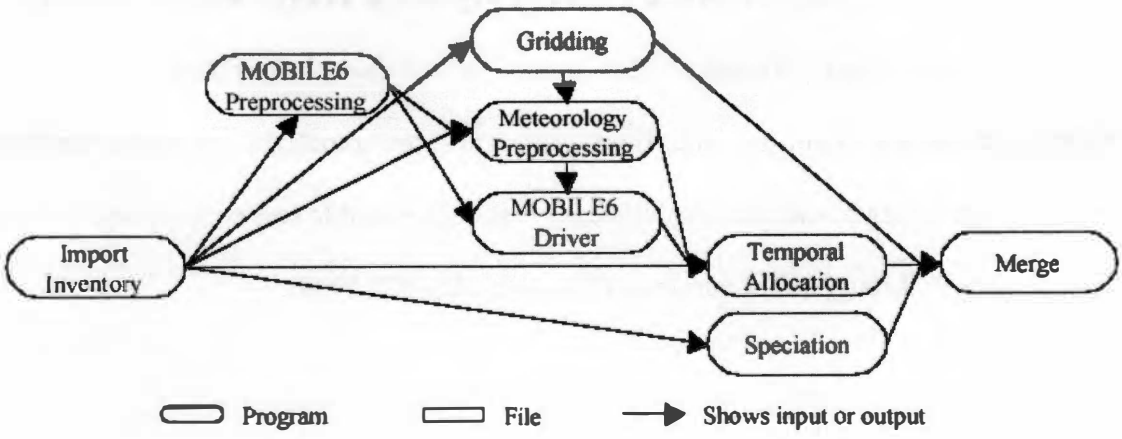


Figure 29 Mobile source processing (SMOKE manual, 2003)

The gridding step also determines how the meteorology data can be averaged over counties, which form "ungridding" factors. The meteorology preprocessing step utilizes these "ungridding" factors and the prognostic meteorology data to calculate county-specific hourly temperatures, which are fed to the MOBILE 6.2 driver to compute hour-specific emissions factors. The temporal allocation step integrates the VMT and emission factors and makes other temporal adjustments to obtain hour-specific emissions for each emission process. The chemical speciation step calculates the chemical speciation factors for each county, road class, vehicle type, emissions process, and pollutant and stores the necessary factors for this transformation. The merge step finally combines the hourly emissions by process, spatial allocation factors, and chemical speciation factors to compute model ready emissions (SMOKE manual 2003).

The intermediate and output files of SMOKE are generated in a format known as Network Common Data format (NetCDF), which in turn is used by the CMAQ air quality model. In programs expected to work in Models-3, the NetCDF files are generated with a library called the Input/Output Applications Programming Interface (I/O API). The advantages of I/O API NetCDF files are 1) they are portable to any computer platform 2) they are small sized binary formatted files 3) they are self-describing files as they contain a header with details about the date, time, grid, and other important file characteristics; and 4) the data are direct-access, which means that each variable can be accessed without the need to scroll through other variables (Houyoux, MCNC 1999).

2.3 Air Quality Models

Air quality models are important and vital tools for regulatory, policy, and environmental research communities. In the United States, Clean Air Act presents a societal mandate to review and manage air pollution levels to protect human health and environment. The US EPA has also set National Ambient Air Quality Standards, which require the development of effective emissions control strategies for pollutants like ozone, particulate matter and nitrogen species. National and regional policies are necessary for reducing and managing the amount of above mentioned pollutants and also the type of emissions that cause acid, nutrient and toxic pollutant deposition to ecosystems at risk. Air quality models are utilized by the EPA to develop emission control strategies to achieve these objectives (Ching, EPA/600/R-99/030, 2003).

The development of exclusive air quality models started in the late seventies. The Urban Airshed Model (UAM) followed by Regional Oxidant Model (ROM) offered Eulerian-based models for ozone. Regional Acid deposition models like the RADM (Regional Acid Deposition Model) were introduced in the eighties. With the passage of Clean Air Act Amendments of 1990, a wide range of additional issues were recognized including visibility, fine and coarse particles, indirect exposure to toxic pollutants such as heavy metal, semi-volatile organic species, and nutrient deposition to water bodies. The existing models were modified at that time to accommodate the new issues (Ching, EPA/600/R-99/030, 2003).

2.3.1 Air Toxics Modeling

The prediction of outdoor air toxics concentrations is a difficult task as the available ambient data are generally sparse and the source based model simulations have uncertainties that result from their formulation and inputs. The best approach in such a situation would be to combine the use of source-based models, to obtain necessary spatial and temporal resolutions, with the use of all available reliable data to minimize the model uncertainties. The three-dimensional time dependent concentrations of air toxics at regional and urban scales can be computed using a 3-D gridded model. Three dimensional gridded models are favored to plume models as the large variety of emission sources (point, area, mobile, and non-road) is more conducive to the use of a 3-D gridded model than a plume model. Also, many plume models used at present are not applicable beyond about 50 km, and air toxics may persist outside such travel distances (Seigneur Christian, 2002).

The various three-dimensional models that have been used to simulate the outdoor concentrations of air toxics are i) Urban Airshed Model IV ii) Regional Modeling System for Aerosols and Deposition iii) Acid Deposition and Oxidant Model iv) Community Multiscale Air Quality Model (Seigneur Christian, 2002).

A brief description, including the features and limitation, of the different types of three-dimensional models is given in this section.

Urban Airshed Model version IV (UAM-IV)

This model which was originally created for ozone simulation is an urban-scale 3-D grid-based. South Coast Air Quality Management District or SCAQMD has used this model

to determine air toxics concentration. The model uses a Universal Transverse Mercator (UTM) horizontal coordinate system. The vertical resolution normally consists of four to six layers that vary in depth with mixing height. The model cannot be used for regional applications as the formulation primarily focuses on the planetary boundary layer and not on free troposphere. Either diagnostic meteorological model or a prognostic meteorological model can be used to create meteorological inputs for this model. Smolarkiewicz algorithm is used to resolve adjectives transport and a constant coefficient is used for horizontal turbulent diffusion. The clouds and convective subgrid-scale transport is not treated by this model. UAM does not simulate any chemistry or chemical reactions while modeling air toxics and the version IV does not treat wet processes or simulate wet deposition (Seigneur Christian, 2002).

Regional Modeling System for Aerosols and Deposition (REMSAD)

This 3-D grid-based model was created to simulate PM concentrations and air toxics depositions at large regional scales over long time periods. The model's horizontal grid structure is based on a latitude/longitude system and the vertical grid structure is based on a terrain-following sigma-pressure coordinate system. The meteorological files used in the model can be obtained from either MM4 and MM5 simulations or Rapid Update Cycle prognostic meteorological model. A modified SMOKE emission processing tool can be used to generate emission files that are compatible with REMSAD. Smolarkiewicz algorithm is used to resolve advective transport and horizontal turbulent diffusion is calculated. When the cumulus clouds are present the convective transport is treated as a subgrid parameterization. So far only five air toxics species: mercury,

dioxins, cadmium, polycyclic organic matter (POM) and atrazine have been modeled using REMSAD. Apart from formaldehyde the model does not treat volatile organic air toxics explicitly. A resistance approach is used to simulate dry deposition of gases and particles, while wet deposition is parameterized for both gases and particles and is a function of the rainfall rate and cloud characteristics (Seigneur Christian, 2002).

Acid Deposition & Oxidant model (ADOM) and its derivative versions

ADOM is a comprehensive 3-D Eulerian model, which was originally created for acid deposition and oxidant simulations. The model was later modified to simulate air toxics concentrations. The Arizona Department of Environmental Quality (ADEQ) supported an air toxics modeling study where concentrations of a number of air toxics were modeled with ADOM over an entire year. The model uses a polar stereographic projection for the horizontal coordinates; the vertical layers are spaced logarithmically with higher resolution in the lowest layers. The model does not use a terrain-following coordinate system and the layer heights are fixed for all the grid cells. ADOM utilizes separate files for area and major point sources with hourly emission. Plume calculations are performed by the model itself. When handling air toxics, a semi-Lagrangian scheme has been used for advective transport and vertical turbulent transport is treated with a K-diffusion algorithm. In the existence of cumulus clouds convective transport is treated at the sub-grid scale. A suitable chemical kinetic mechanism should be added to model volatile and semi-volatile toxic organic compounds at urban and regional scale (Seigneur Christian, 2002).

Models-3 Community Mulitscale Air Quality Model (CMAQ)

Models3/CMAQ, created under the leadership of EPA's Office of Research and Development, presents the overall frame work including a graphical user interface. CMAQ uses a universal coordinate system for the horizontal and vertical coordinates. For the horizontal coordinate a Lambert conformal comic projection, a universal transverse Mercator projection, or a polar stereographic projection can be used. The Lambert conformal conic projection is appropriate for mid latitudes and is also consistent with the grid structure of the models normally used to create meteorological inputs for CMAQ. A terrain-following sigma-pressure system is considered for vertical coordinate. This coordinate depends of time for hydrostatic simulations and time independent for non-hydrostatic modeling. All the input files taken in by the model and the output files generated are in network common data form (netCDF), which makes the files machine independent. A prognostic meteorological model is used to create meteorological inputs for the model. At present, CMAQ is compatible with the MM5 and RAMS models. The Sparse matrix Operator Kernel Emissions (SMOKE) modeling system generates hourly gridded emissions required by CMAQ model. The emission processor SMOKE performs plume rise calculations for major point sources and CMAQ takes a single 3-D emissions file as input. The model is flexible with several options for modeling certain processes. Both piecewise parabolic method and Bott algorithm can be used to simulate advective transport. The vertical turbulent transport is simulated using K-diffusion algorithm and when cumulus clouds are present convective transport is modeled at the subgrid scale (Seigneur Christian, 2002).

2.3.2 CMAQ air toxics version

The three dimensional model used in this thesis is the CMAQ air toxics model. The air toxic is the latest version of CMAQ model and can be obtained from the EPA only up on request. This is the first EPA developed model which exclusively addresses the toxic chemical reactions in the atmosphere.

The main functions of the Community MultiScale Air Quality modeling system are to improve the environmental management community's ability to evaluate the effect of air quality management practices for multiple pollutants for multiple scales and to improve the scientist's capacity to better probe, understand, and simulate chemical and physical interactions in the atmosphere. The US EPA developed the CMAQ system mainly to meet the challenges posed by Clean Air Act Amendments of 1990 and the requirement to address the complex relationships between pollutants (Ching, EPA/600/R-99/030, 2003).

The CMAQ is a multi-pollutant, multiscale air quality model that has state-of-science techniques for modeling all atmospheric and land processes that affect the transport, transformation, and deposition of atmospheric pollutants and their precursors on both regional and urban scale. CMAQ air quality modeling system integrates output fields from emissions and meteorological modeling systems and several other data source through special interface processors into the CMAQ Chemical Transport Model (CCTM). The chemical transport modeling for multiple pollutants on multiple scales is executed by the CCTM program (Ching, EPA/600/R-99/030).

The main components of CMAQ air quality model are

- Initial Conditions (ICON) and Boundary Conditions (BCON) Processor
- Photolysis Processor (JPROC)

- Chemical Transport Model (CCTM)

Initial Conditions (ICON) and Boundary Conditions (BCON) Processor

The ICON and BCON processors have been developed to process data as automatically as possible. It generates Initial Conditions and Boundary Conditions for each model species, which include gas-phase mechanism species, aerosols, non-reactive species and tracer species. The CCTM will attempt to filter ICs and BCs for each species being modeled from the input files. If a species is not present in the file, the CCTM will automatically set its ICs and BCs to a minimum threshold limit (zero). Any record on the IC or BC file for a species that is not being modeled will simply be ignored by the CCTM. The ICON processor creates species concentrations for every cell in the modeling domain, while the BCON processor generates species concentrations for the cells immediately surrounding the modeling domain. The output from both processors is written to standard Models-3 Input/Output Application Programmer Interface files: three dimensional gridded files for ICs and three dimensional boundary files for BCs (Gipson, EPA 030, 2002).

Photolysis Processor (JPROC)

A number of chemical reactions in the atmosphere are initiated by the photo dissociation of numerous trace gases. In order to make an accurate prediction of the effects of air pollution, good photo dissociation reaction rate estimates must be made. Preprocessor JPROC computes a table of clear-sky photolysis rates for a specific date. The data is dimensioned by latitude, altitude, and time. JPROC is flexible to utilize any

extraterrestrial radiation data distribution specified by the user. The current method for computing photolysis rate, which was derived from RADM uses a preprocessor to compute a look-up table and a subroutine within the chemistry transport model to interpolate J-values and apply a cloud-cover correction (Roselle, EPA/600/R-99/030, 2002).

Chemical Transport Model (CCTM)

The CCTM models the relevant and major atmospheric chemistry, transport and deposition processes involved through out the modeling domains. The various options available in this model include gas phase chemistry mechanisms, numerical solvers for the mechanism, options for horizontal and vertical advection schemes, algorithms for fine and coarse particulate matter predictions, photolysis rate, and plume-in-grid approach (Ching, EPA/600/R-99/030, 2003). The transport process in the atmosphere mainly consists of advection and diffusion, with the exception of the mixing of pollutants by the parameterized subgrid-scale clouds. In order to provide the CMAQ system with multiscale ability, both advection and diffusion transport processes were formulated in conservation form for the generalized coordinate system (Byun, EPA-030, 2003). Reactions in the gas-phase are represented in air quality models by means of chemical mechanisms (Byun, EPA-030, 2003). The air toxics version of CMAQ has the ability to handle both CB IV and SAPRC 99 mechanisms. The reaction of each toxic species is handled in detail by this model. To facilitate changing mechanisms an adding new species, CMAQ system contains a generalized chemical mechanism processor (Byun, EPA-030). The model contains algorithms to treat subgrid scale physical and chemical

processes impacting pollutant species in plumes emitted from selected Major Elevated Point Source Emitters. The PinG modules model plume rise and growth, and the relevant dynamic and chemical reaction processes of subgrid plumes (Ching, EPA/600/R-99/030, 2003). Detail descriptions of clouds are necessary in air quality modeling due to their vital role in the atmospheric pollutant transport and chemistry processes. Clouds have both direct and indirect impact on the pollutant concentrations; they modify concentrations via aqueous chemical reaction, vertical mixing, and wet deposition removal process (Ching, EPA/600/R-99/030, 2003). The model simulates deep convective clouds and shallow clouds using algorithms as applied in RADM for 39 and 12 Km resolutions. At 4 Km resolution, the clouds are generally resolved, and open type cloud dominates (Ching, EPA/600/R-99/030, 2003).

2.4 Region under consideration

In this thesis the Houston region in the Texas state is considered as a case study. For more than 20 years the US EPA has classified the Houston region as a "severe non attainment area" for ground level ozone as the region has consistently failed to meet the one-hour federal health standard for ozone. The non-attainment area includes eight counties: Harris, Galveston, Brazoria, Fort Blend, Waller, Montgomery, Chambers, and Liberty (GHASP, 2002). The region also emits a significant amount of toxic pollutants into the atmosphere. Formaldehyde and acrolein concentrations regularly reach levels at which acute health effects like respiratory distress and eye irritation are caused upon immediate exposure (GHASP, 2003). A number of pollutants react chemically to form ozone, particularly nitrogen oxides (NOx), which are products of combustion, and

volatile organic compounds like ethylene and butadiene. Formaldehyde plays a significant role in Houston's unusually rapid ozone formation (GHASP, October 2003). The days for which emissions are processed and pollutants are modeled are August 22nd to September 1st 2000. These days were selected as they coincide with a high ozone episode. Figure 30 shows the non attainment counties in the Houston area of Texas. The Houston city is located in the Harris County. Figure 31 shows the effect of air pollutants on the visibility in Houston city.

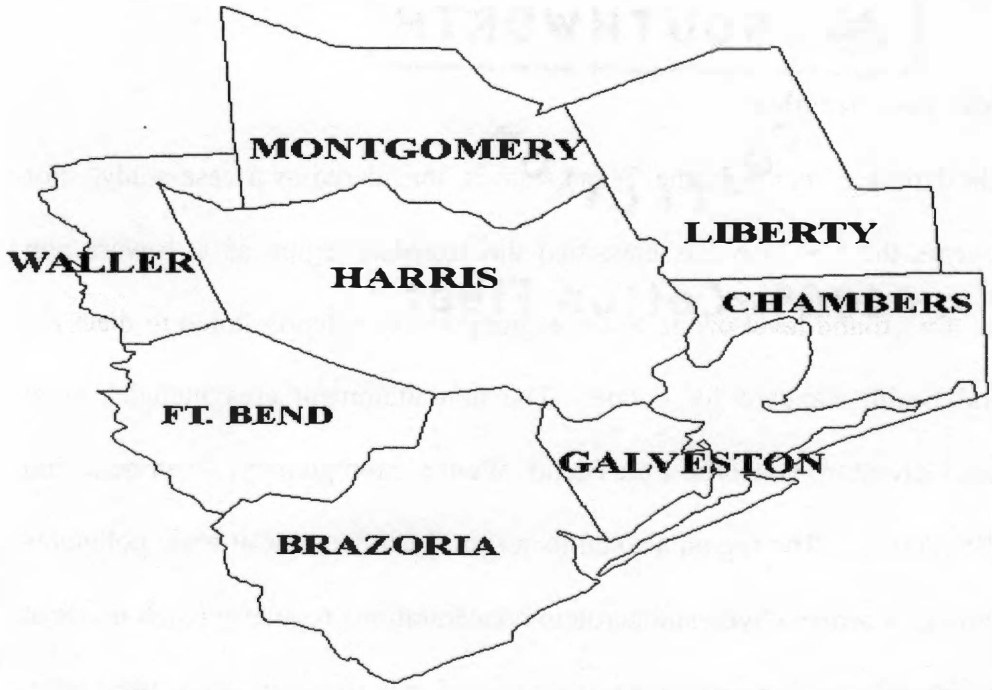


Figure 30 Ozone non attainment counties in the Houston region, Texas (Hamilton 96)

Clear day **Hazy day**

Figure 31 Air Pollutants effect on the visibility in Houston city (Texas Air Quality Study, 2000)

CHAPTER 3

METHODOLOGY

The methodology followed in this thesis is broadly divided into three steps. These are

- Emission Inventory Preparation
- Emission processing with SMOKE 2.0
- Pollutant modeling with CMAQ air toxics model

Each of these steps are discussed in detail in this chapter

3.1. Emissions Inventory Preparation

In this step the emission inventory for the 15 toxic species (considered in this thesis) emitted in the state of Texas was prepared. The fifteen toxic species considered were acrolein, benzene, butadiene, perchloroethylene, trichloroethylene, vinyl chloride, methylene chloride, ethylene dibromide, ethylene dichloride, ethylene oxide, acetaldehyde, carbon tetrachloride, chloroform, acrylonitrile, and propylene dichloride.

Emission Inventories

The toxic emission inventories used were National Emission Inventory (NEI) and Toxic Release Inventory (TRI). The TRI for the year 2000 (year considered for a case study in this thesis) was obtained from the US Environmental Protection Agency (EPA); the National Emission Inventory, which is developed once in three years, was not available for the year 2000 hence the latest available NEI (1999) was considered. The use of growth factors to project NEI emissions for the year 2000 from the 1999 National

Emission Inventory was considered. However EPA (Madeline Strum) recommended the use of NEI- 1999 for the year 2000 as a number of emission records in the latest available inventory were actually recorded in the year 2000 and the use of growth factors would be appropriate only while projecting emissions after a five or more year period. The emissions for the state of Texas were extracted from both the inventories (NEI – 1999, TRI -2000) and were filtered for the 15 toxic species considered in this thesis. The final refined NEI and TRI contained the 15 toxic species emissions in the state of Texas.

National Emission Inventory

NEI contains emissions from point, area, non-road and mobile sources. The point source inventory has all the details, including the stack parameter values, required for pollutant modeling. The inventory, which is updated every three years, also has criteria pollutants emissions.

Toxic Release Inventory

The Toxic Release Inventory contains emission values for point sources only. The inventory, which is updated every year, does not contain key facility details like stack parameters required for pollutants concentration modeling. In order to overcome this limitation of the TRI, the Texas AFS table provided by the Texas Commission on Environmental Quality (TCEQ) was used. The Texas AFS table also known as AIRS (Aerometric Information and Retrieval System) Facility Subsystem database contains the stack parameter details of all the facilities in the state of Texas. The average of the stack parameter values given in these tables were considered for facilities, which did not have

any stack parameter values in the TRI table. Unlike the default stack parameters generated by the EPA, the AFS stack parameters are specific for the state of Texas and hence are more appropriate for the case under study. The combination of AFS and TRI is shown in Figure 32.

Difference between the two inventories

The area, point and non-road source emissions were obtained from the NEI 1999, while for the point source emissions both NEI 99 and TRI 2000 were considered. On comparing the two point source inventories it was found that the NEI 99 had greater number of emission records than TRI 2000 and for a number of facilities NEI 99 had relatively lesser emission values than TRI 2000. The difference was significantly evident in species like 1, 3-butadine, benzene, acrolein etc.

Merging of Inventories

To overcome the above difference the two point source inventories were merged together. During the merge process the following rules were applied

I. No double counting - When the same facility record with the same emission value was found in both the inventories, only one record (NEI) was considered in the final inventory.

II. Higher emission considered - When the same facility record with different emission values was found in both the inventories, the record with higher emission value was considered for each pollutant. This was done to account the worst possible case, where the higher emission value is more accurate.

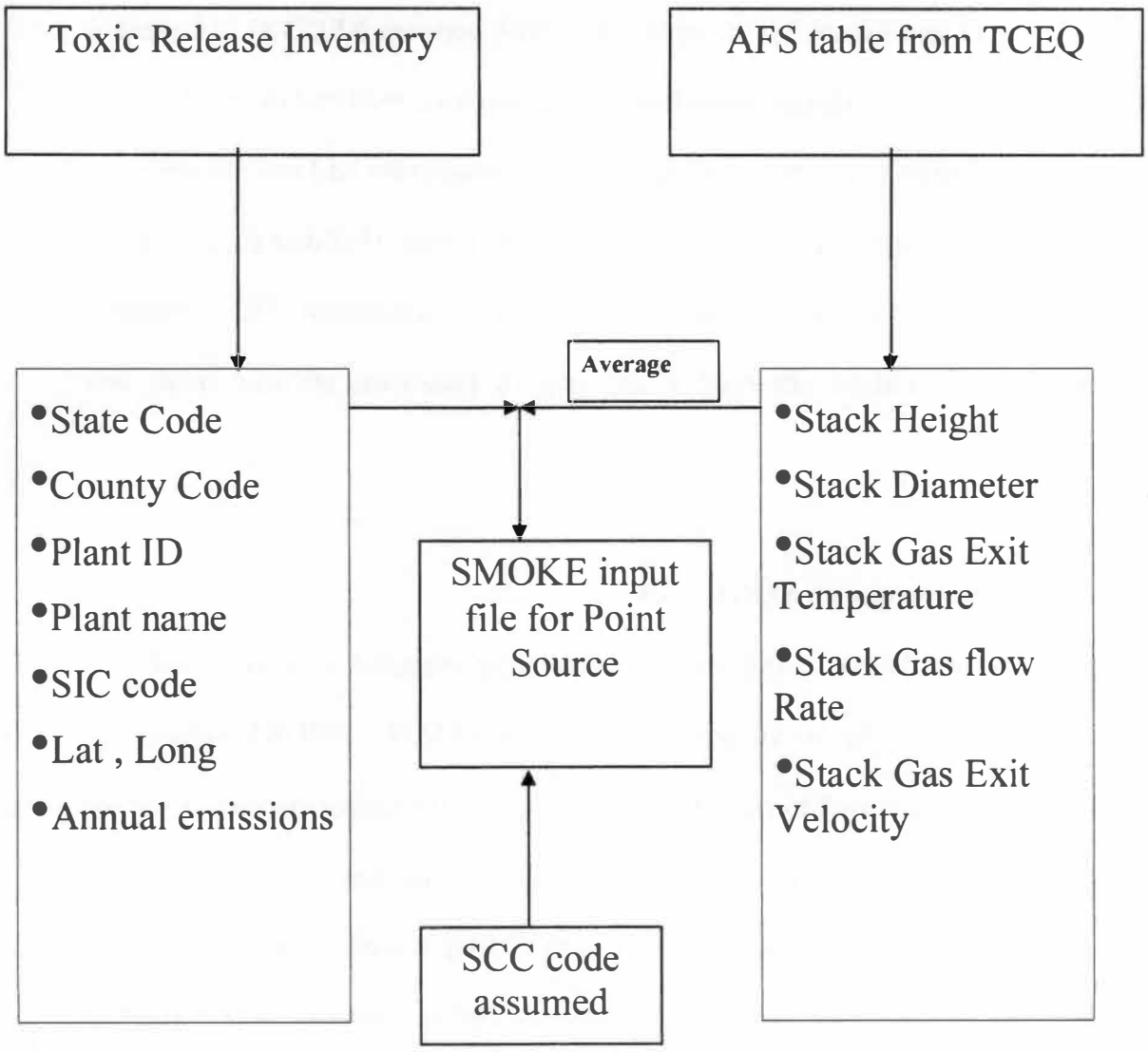


Figure 32 Combining AFS table values with Toxic Release Inventory

III. Addition of records - Facilities which were found TRI but were not found in the NEI were added to the final merged inventory

The final merged inventory contained the total point source emission in the state of Texas. Figure 33 and Figure 34 shows the difference between NEI, TRI and merged point source inventory for eleven of the fifteen toxic species considered in this thesis. It can be observed that there is a considerable difference between the NEI and merged point source inventory for most of the toxic species analyzed. Figure 35 shows the percentage increase in the point source emissions of NEI after merger with TRI emissions. Significant increase can be observed in the case of butadiene, ethylene oxide and trichloroethylene.

3.2 Emission Processing with SMOKE 2.0

In this step the resolution of the emissions inventory prepared was converted to a resolution recognizable by an air quality model like CMAQ. SMOKE version 2.0 emission processor was used to perform the above task. The output obtained from the processor was used to examine the distribution of toxic emissions in the region under study. The output was further used as an input to CMAQ air toxics model in order to predict the concentration of air toxics in the region. The key procedures performed in emission processing stage are discussed in this section.

Creation of input file

The four types of emission inventories (point, area, non-road, mobile) were organized and positioned in a format recognizable by SMOKE 2.0 emission processor.

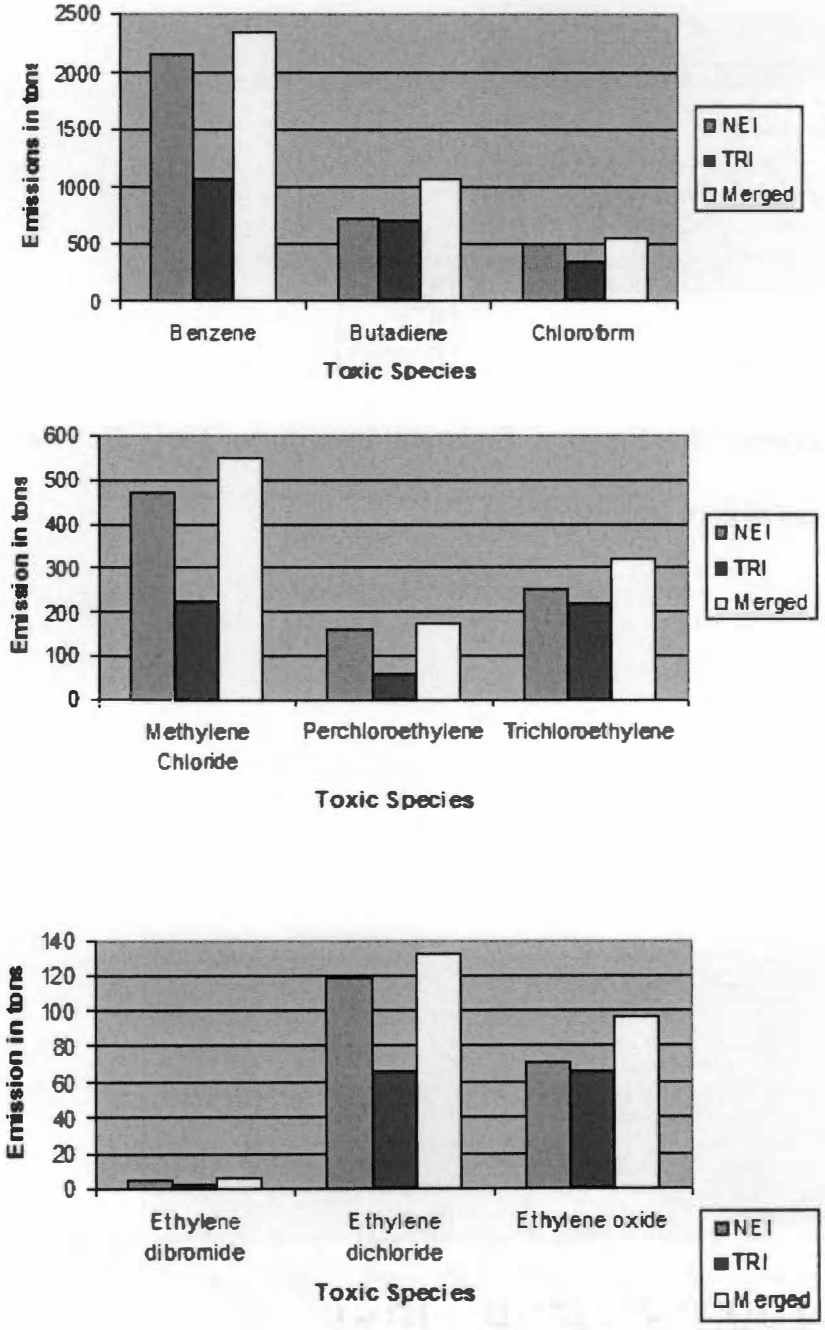


Figure 33 Comparison between the National Emission Inventory, Toxic Release Inventory, and Merged Point source Inventory

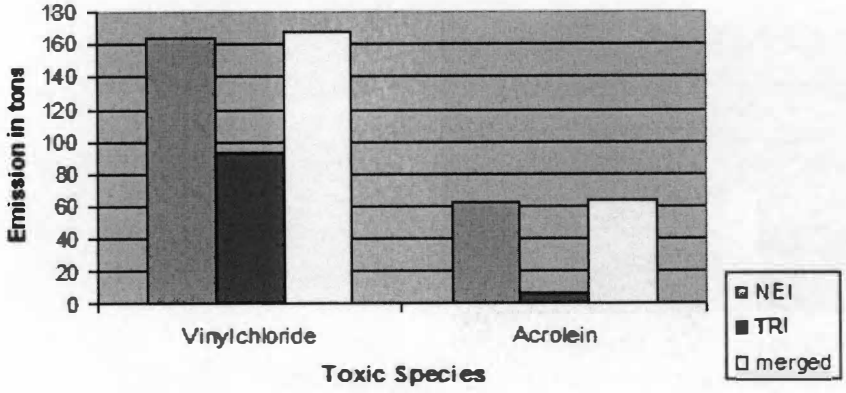


Figure 34 Comparison between the National Emission Inventory, Toxic Release Inventory, and Merged Point source Inventory – II

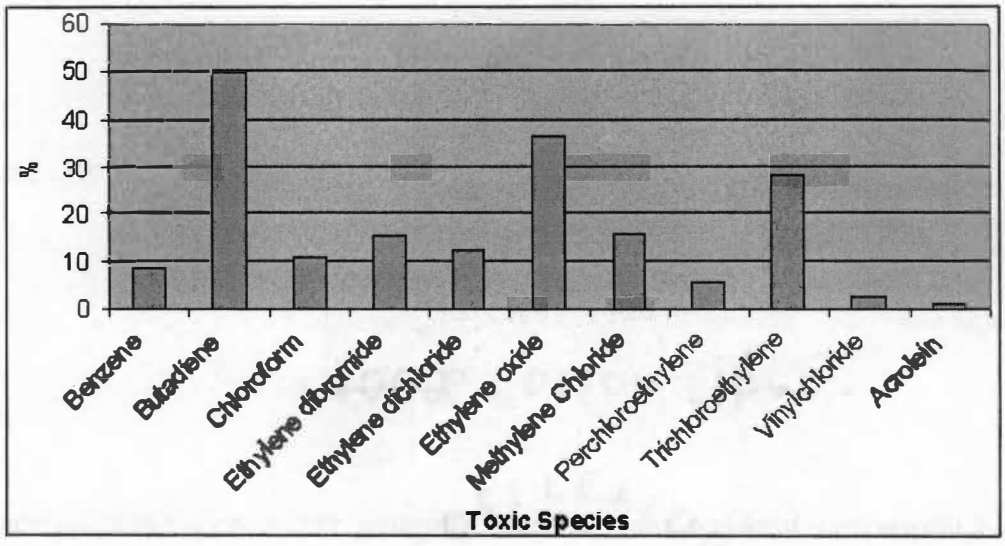


Figure 35 Percentage increase in the point source NEI emissions after merger with TRI

The formatted files were used as an input to the emission processor. The point, area and non-road emission input files were developed in IDA format, while the mobile source emission input file was created in TOXIC format. Both IDA and TOXIC formats were developed following the instructions given in the SMOKE manual.

Grid coordinates

The emissions were processed using a 4Km X 4Km grid, with coordinates focusing on the Houston region, Texas.

Time period

The toxic species considered were processed for 11 days starting from August 22nd, 2000 to September 1st, 2000. This particular period was chosen as it coincides with the peak ozone season in the region.

Meteorology

The MM5 outputs for the above dates (August 22nd, 2000 to September 1st, 2000) were obtained from the University of Houston, Texas. The latest version of the MCIP program was run using the MM5 outputs and the meteorology files required for emission processing were generated.

Number of layers

The number of layers considered in the point source processing was 23. This number was selected after determining the number of layers in the meteorology file.

Surrogate files

The surrogate files for area source processing were generated by the University of Houston, Houston. Based on the surrogate files the annual emissions in the state were distributed among the counties in the region under study. The control matrix is not considered for this case study as no projection of future year emissions is done.

Chemical Mechanism

The chemical mechanism considered for processing toxics was CB IV mechanism. The public version of SMOKE 2.0 does not have the capability to process toxics with SAPRC-99 mechanism. A notable CB IV speciation which can be observed from the cross reference files is the conversion of benzene to paraffin and non-reactant species. The primary benzene emission is split by the processor into three parts one part is converted to paraffin emissions, the second part is transformed into non-reactant (NR) species and the third part stays as benzene.

Biogenic sources

The major toxic species considered in this thesis for analysis are not emitted by biogenic source; hence the biogenic source processor is ignored in this thesis.

Emission processing

The point, area, mobile and the non-road sources were processed separately with the above conditions as the initial setup. The outputs obtained from all the four programs were merged with the merge processor. The above process was repeated for all the eleven days considered in this thesis. The 11 merged outputs obtained from this process were used for analyzing the distribution of toxic emission in the region. The outputs were also used as an input to concentration predicting air quality models like CMAQ.

3.3 Pollutant modeling with CMAQ air toxics model

The processed outputs generated by SMOKE 2.0 emission processor were used as an input to predict the concentration of toxic species considered. The key stages of this process and the conditions under which the model was run are discussed below. The performance of the model was analyzed by comparing the predicted concentration with values recorded by monitor stations in the region. The meteorology files generated by MCIP for emission processor SMOKE were used for running this model. The grid scale used was 4KM X 4KM and the number of layers selected for processing was 23.

The chemical mechanism considered in this model was extended CB IV. This mechanism was selected in order to be consistent with the set up of SMOKE emission processor output. The CMAQ air toxic model comprehensively deals with the toxic reaction occurring in the atmosphere. The model has well defined speciation reaction for most of the toxics, which are taken into account while generating final concentration output. Some of the key speciation includes reaction of primary acrolein with OH in the atmosphere to form formaldehyde, acetaldehyde, paraffin, XO2, C2O3, and HO2;

reaction of 1, 3-butadiene with OH to form formaldehyde and acrolein; reaction of acetaldehyde with OH and NO3. The reactions in the model were created by Jerry Gipson of EPA and were based on the photochemical Kinetics Mechanism for Urban and Regional Scale Computer Modeling (Gipson, 1989). Benzene in the model is not defined by the extended CB IV mechanism, but it does have an outside the mechanism reaction. Benzene reacts in the model with atmospheric OH to form a species called BZIPERO2 (MCM, 2004). The toxic reactions included in the extended CB IV mechanism of the model are listed in Appendix B.

The four major programs of the model which were run to predict concentrations are

- Initial condition processor
- Boundary condition processor
- Photolysis processor
- Chemical transport model

Initial condition processor (ICON)

The initial condition or the ICON processor was run with a setting that the initial concentration of all the toxic species considered was zero. This assumption was suggested by the EPA (Dr. Bill Hutzell), as unlike criteria pollutants the initial profile for toxic species is still under development. The output generated from this processor was used while running the CCTM program for the first (August 22nd, 2000) of the eleven days considered. Due to the assumption that initial concentration of toxics are zero the results obtained from the first three or four days of the model run are normally not used

for analysis as there is bound to be a significant difference between the observed and predicted values.

Boundary condition processor (BCON)

The boundary or BCON processor was run for a 4Km X 4Km grid coordinate. For all the toxic species considered the boundary condition was set to zero (as suggested by the EPA). The 4 Km grid was used in this thesis to obtain a fine resolution of the concentration distribution. The output, which contains the boundary profile for a 4 km grid is used while running chemical transport model for all the eleven days of study.

Photolysis processor (JPROC)

The JPROC or photolysis processor was run for each of the 11 days considered starting from August 22nd, 2000 to September 1st, 2000. The clear sky photolysis rate was computed and the output for each day was used while modeling concentration for that particular day.

Chemical transport model (CCTM)

The chemical transport model integrates the output of SMOKE 2.0 emission processor with the outputs from ICON, BCON, and JPROC programs and processes it. The program generates hourly concentration of toxic species considered as an output. The model was run for the days August 22nd, 2000 to September 1st, 2000.

When modeling the first day's concentration the ICON profile output was used along with the outputs from JPROC, BCON and SMOKE 2.0. From the second day the "cctm"

output from the previous day was used instead of the ICON processor output (i.e.) the "cctm" output of Aug 22nd (previous day) was used as the initial condition input for Aug 23rd (current modeled day) and so on. The output obtained from the model was compared with hourly concentration measured by monitor station, located in the region under study, during the same period of study (Aug 22nd to Sept 1st, 2000).

CHAPTER 4

RESULTS AND ANALYSIS

The outputs obtained from SMOKE emission processor and CMAQ air toxics model are presented and discussed in this chapter. In the case of SMOKE, results of the fifteen toxic species are shown in this section. An analysis on the basis of percentage contribution of total emission by each source type was also done and is discussed in this section.

4.1 SMOKE emission processor outputs

The SMOKE processor generated outputs for point, mobile, area and non-road sources. The merged output was also obtained for each day from the four individual source outputs. Of the eleven days considered for each species, the day on which highest emission values were observed was selected for discussion in this thesis. For each toxic species the processed output from area, mobile, non-road, and point sources are displayed along with the merged source output. For each individual source or sector the hour at which peak emissions were observed on the day considered is displayed. The time represented in the figures is in GMT (Greenwich Mean Time).

From the results of SMOKE it can be noted that mobile source contributes to only four of the fifteen species considered. These are Acrolein, Benzene, Butadiene and Acetaldehyde. From Figure 36 it can be observed that a large amount of mobile source acrolein emissions are released in Harris County, while significant amount of area source acrolein emissions are emitted from Brazoria County. From Figure 37 it can be noted

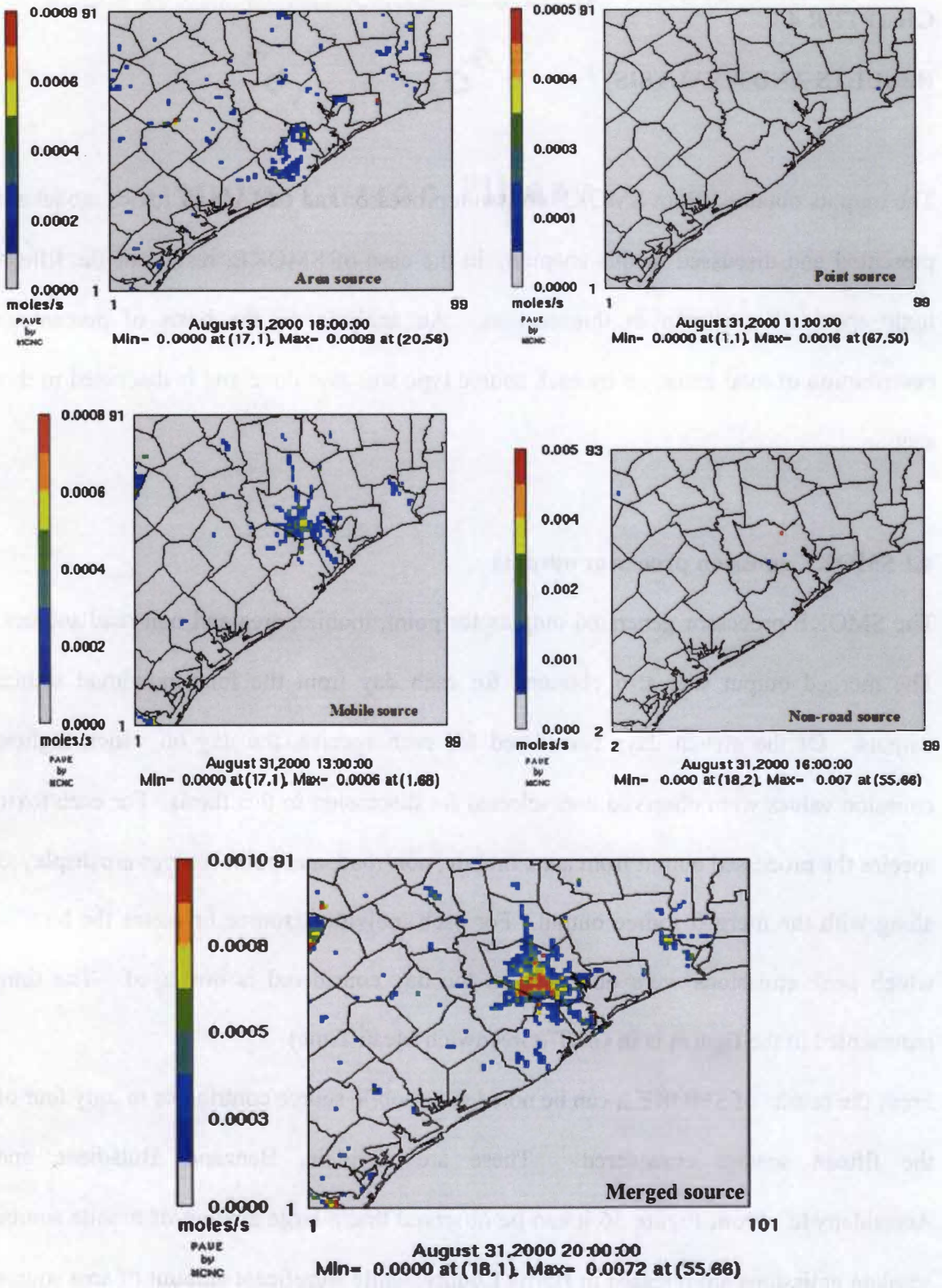


Figure 36 Acrolein Emissions Distribution

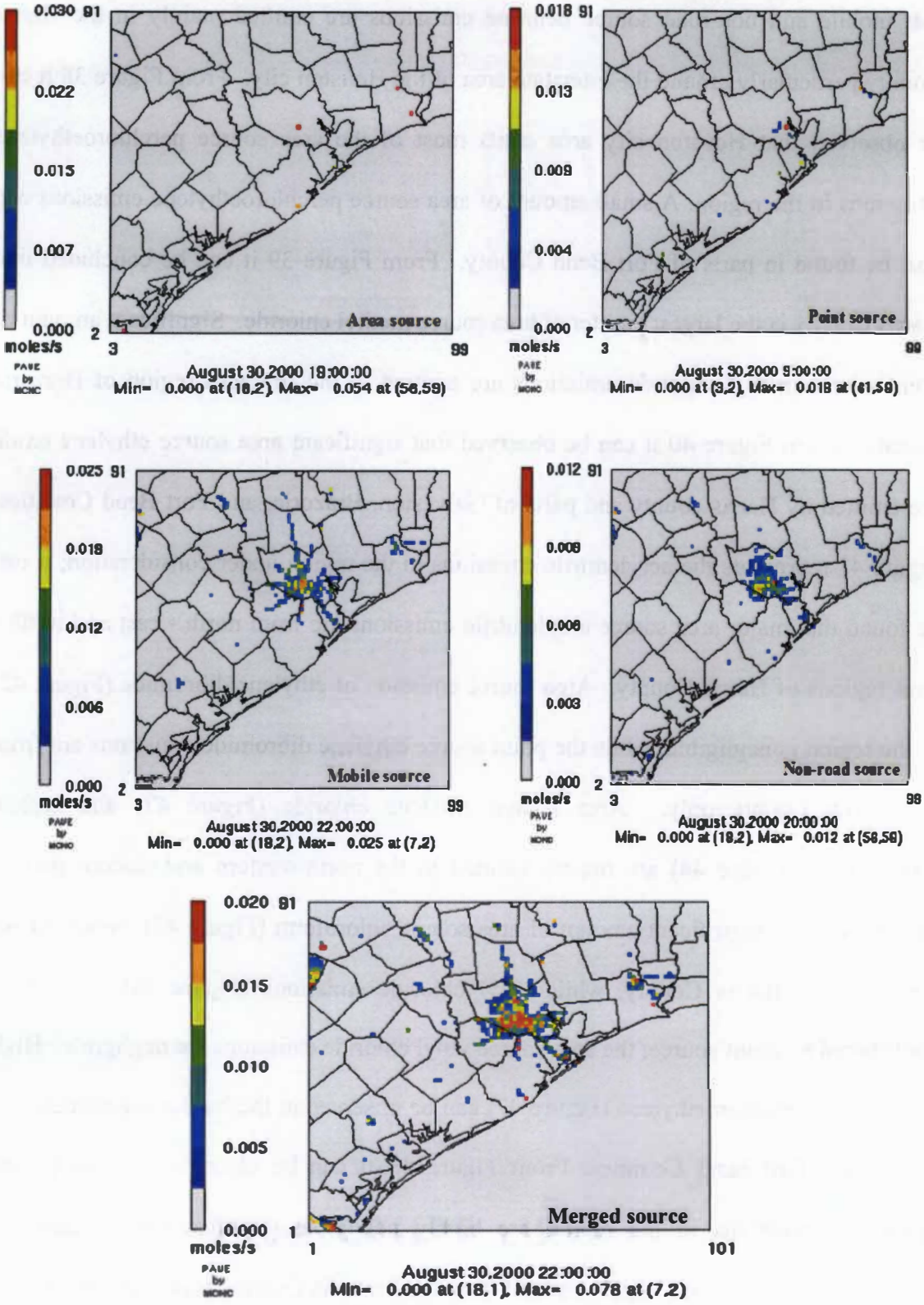


Figure 37 Benzene Emissions Distribution

that mobile and non-road source benzene emissions are emitted mainly in the Harris County particularly around the interstate area of the Houston city. From Figure 38 it can be observed that Houston city area emits most of the area source perchloroethylene emissions in the region. A small amount of area source perchloroethylene emissions can also be found in parts of Fort Bend County. From Figure 39 it can be concluded that Harris County is the largest emitter of area source methyl chloride. Significant amount of point source methyl chloride emissions are emitted in the southern region of Brazoria County. From Figure 40 it can be observed that significant area source ethylene oxide are emitted by Harris county and parts of Galveston, Brazoria, and Fort Bend Counties. Figure 41 represents the acrylonitrile emissions in the region under consideration; it can be found that major area source acrylonitrile emissions are from north - east and north - west regions of Harris County. Area source emission of ethylene dibromide (Figure 42) in the region is negligible, while the point source ethylene dibromide emissions are from the Harris County only. Area source ethylene chloride (Figure 43) and carbon tetrachloride (Figure 44) are mainly emitted in the north-western and eastern part of Harris County. Significant amount of area source chloroform (Figure 45) emissions are emitted from Harris County, while vinyl chloride emissions (Figure 46) are mainly contributed by point source; the area source vinyl chloride emissions are negligible. High emissions of trichloroethylene (Figure 47) can be observed in the border region between Harris and Fort bend Counties. From Figure 48 it can be observed that propylene dichloride emissions in the region are highly negligible. Area source butadiene emissions (Figure 49) are largely emitted from the Brazoria County; lesser amount of

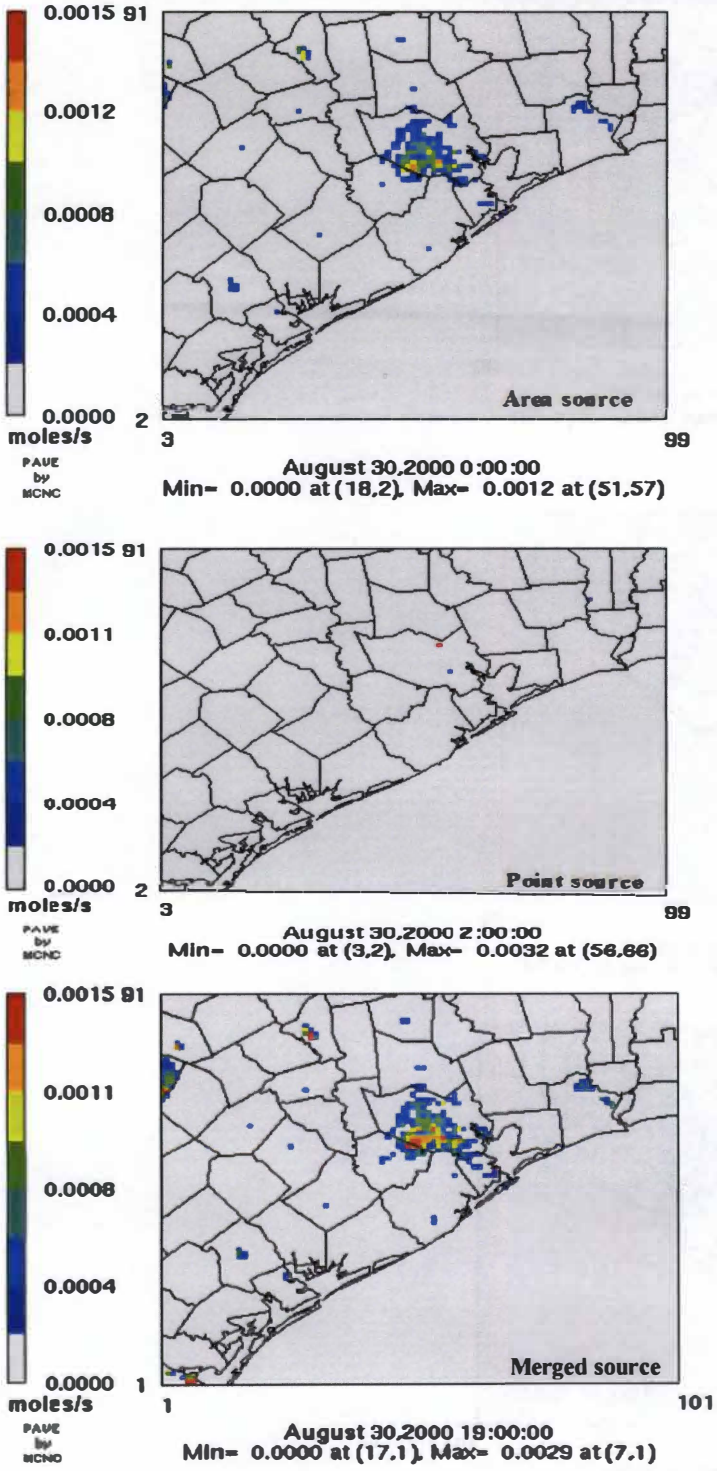
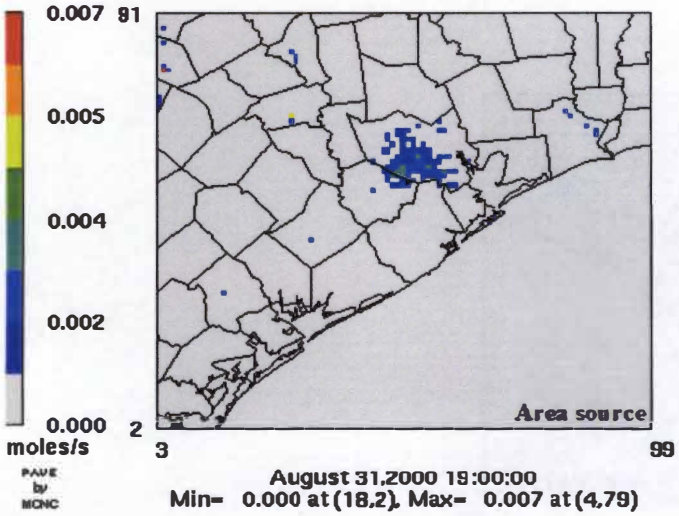
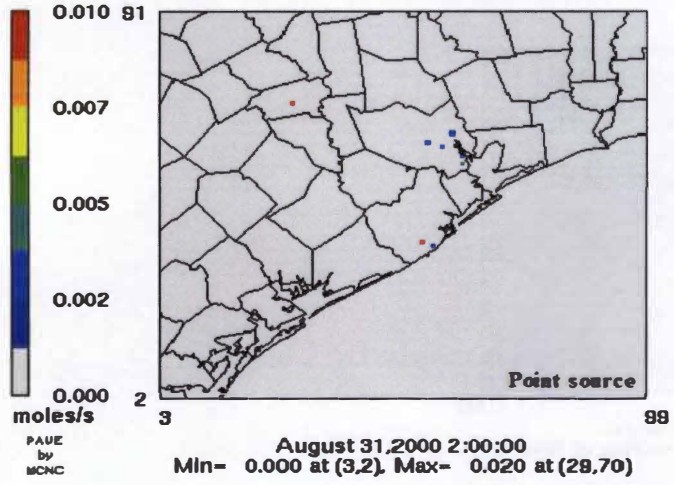


Figure 38 Perchloroethylene Emissions Distribution





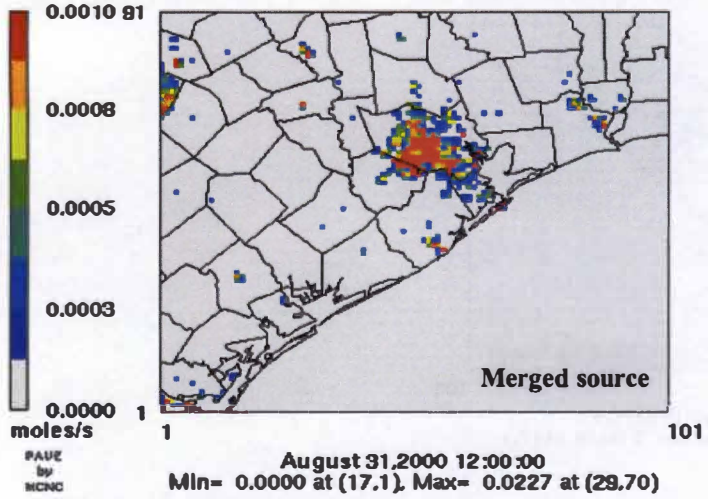
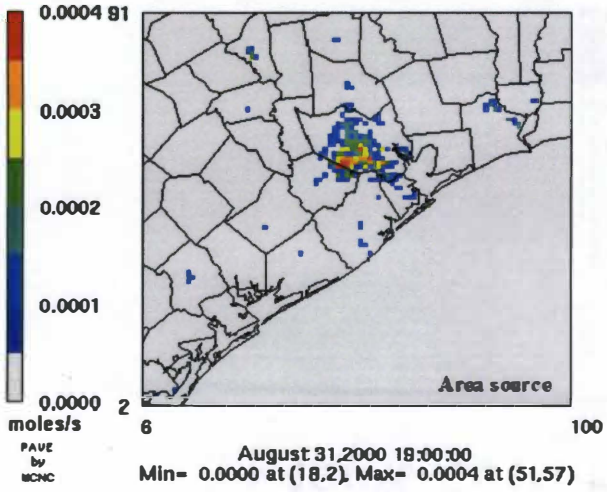
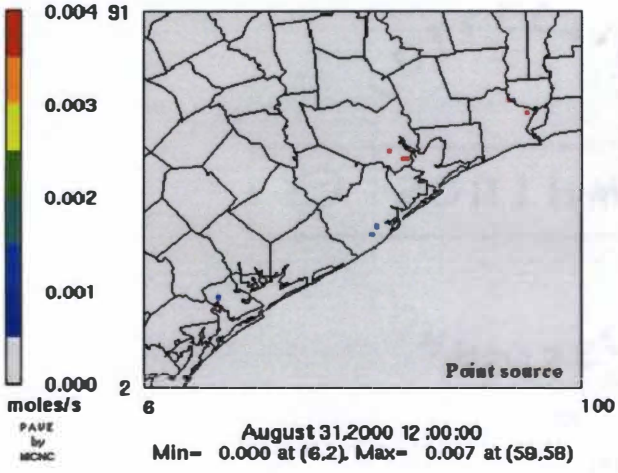


Figure 39 Methyl Chloride Emissions Distribution





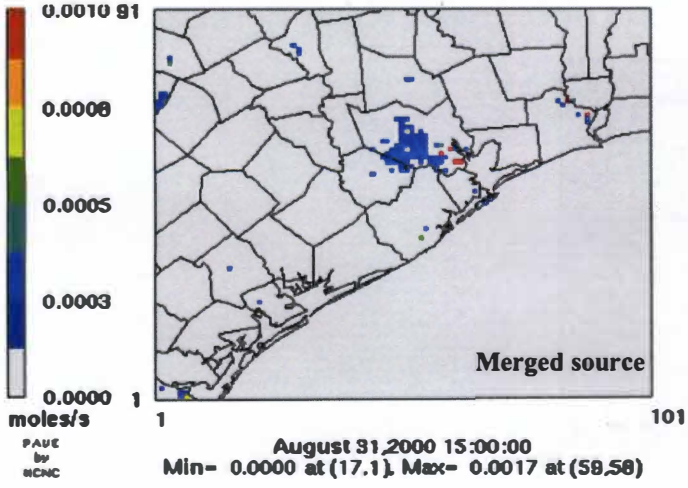


Figure 40 Ethylene oxide Emissions Distribution

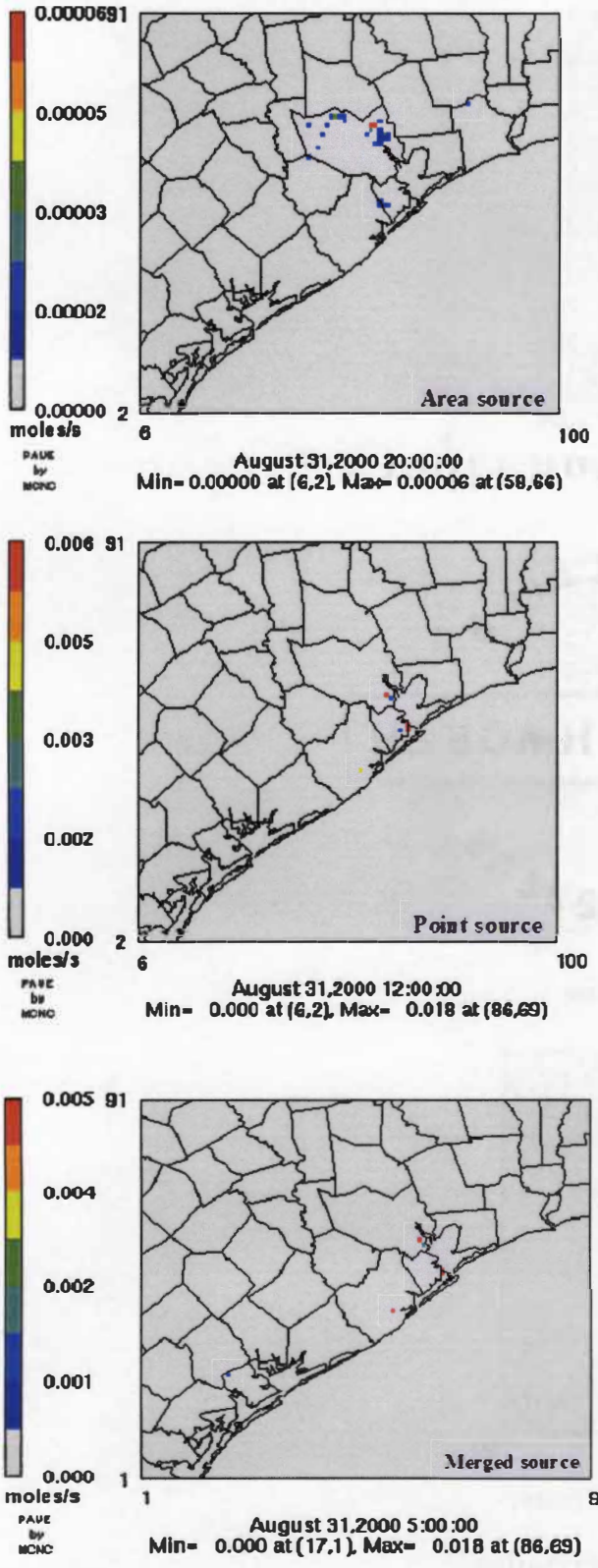
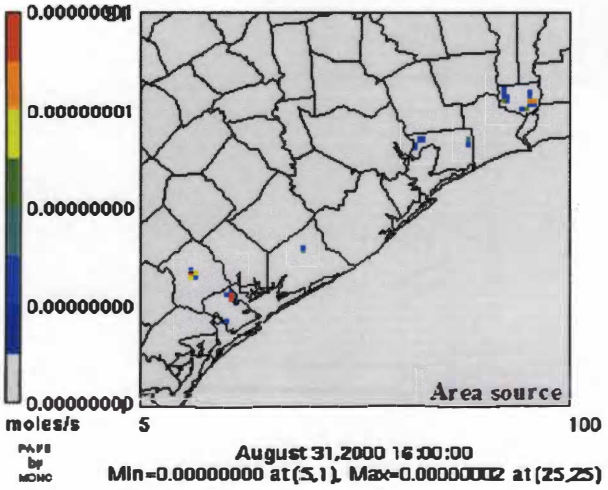
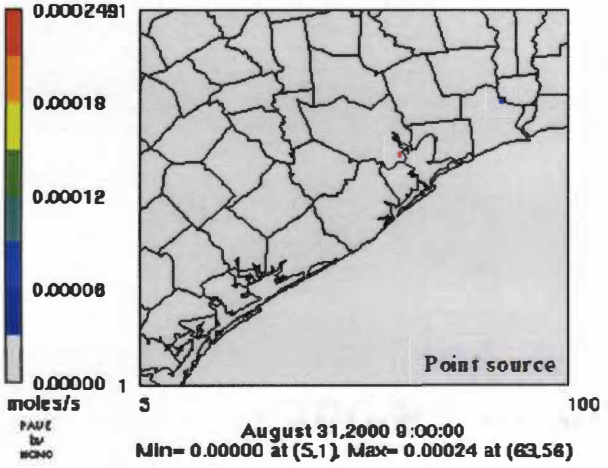


Figure 41 Acrylonitrile Emissions Distribution





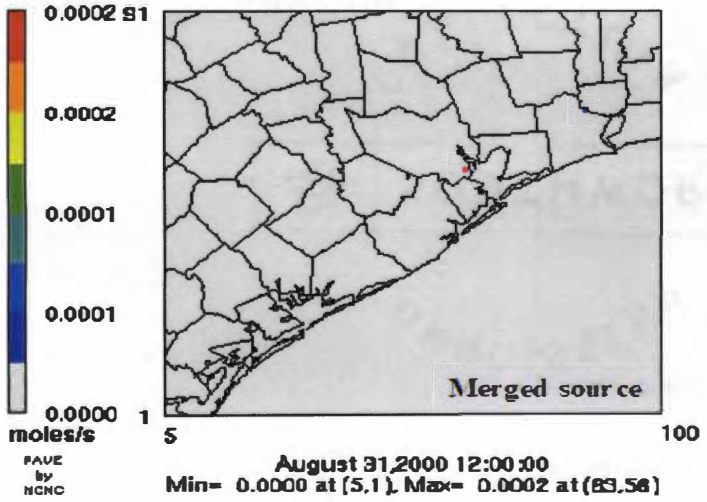
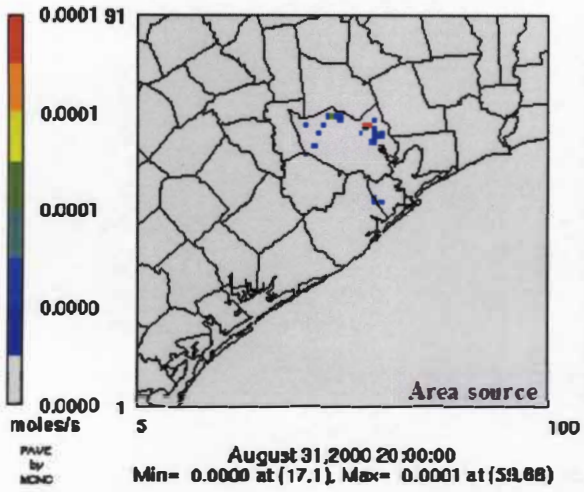
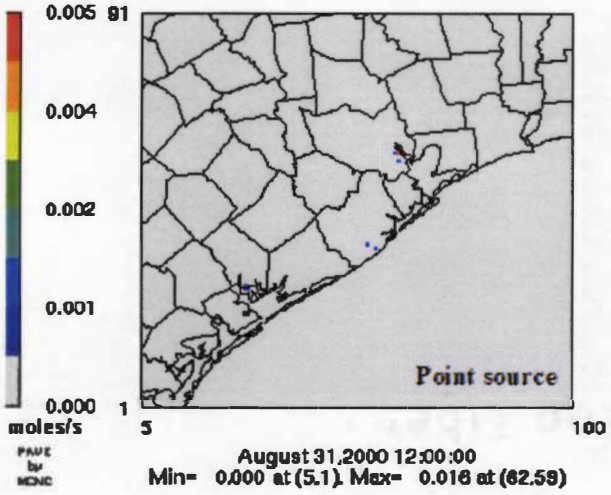


Figure 42 Ethylenedibromide Emissions Distribution





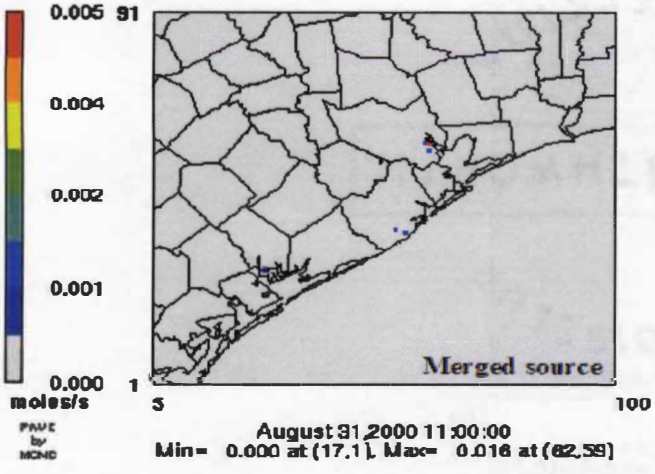


Figure 43 Ethylene Dichloride Emissions Distribution

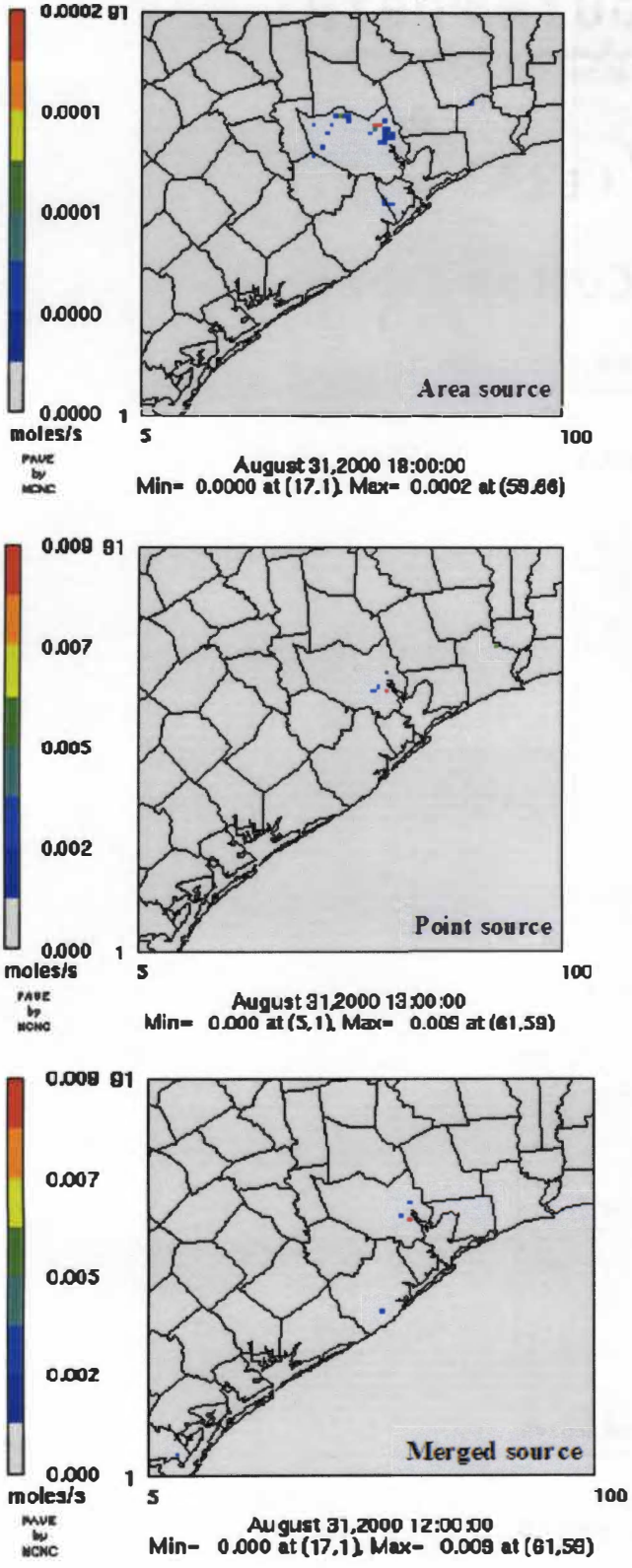
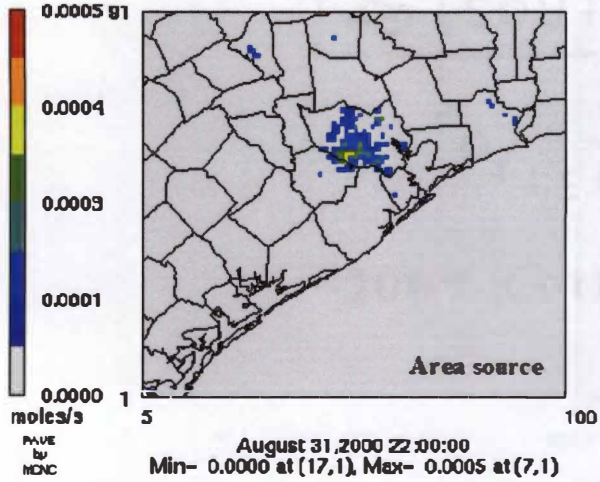
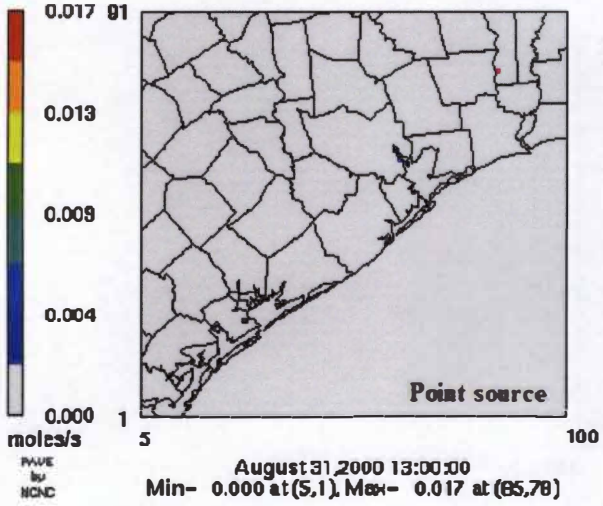


Figure 44 Carbon Tetrachloride Emissions Distribution





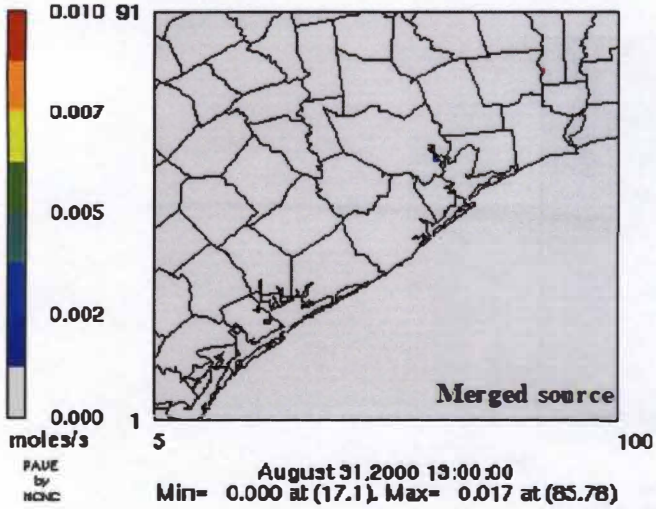
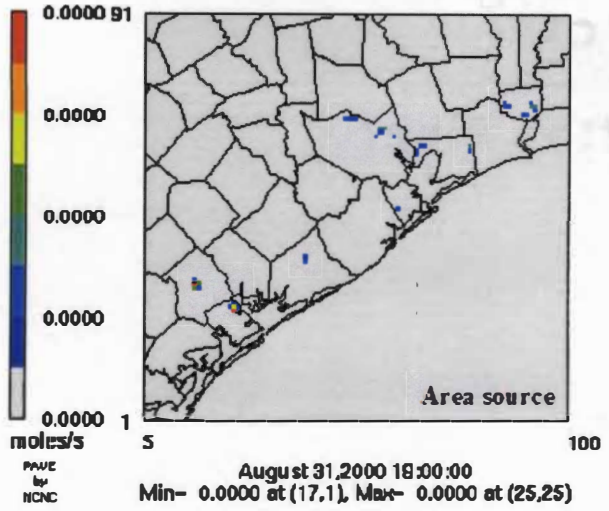
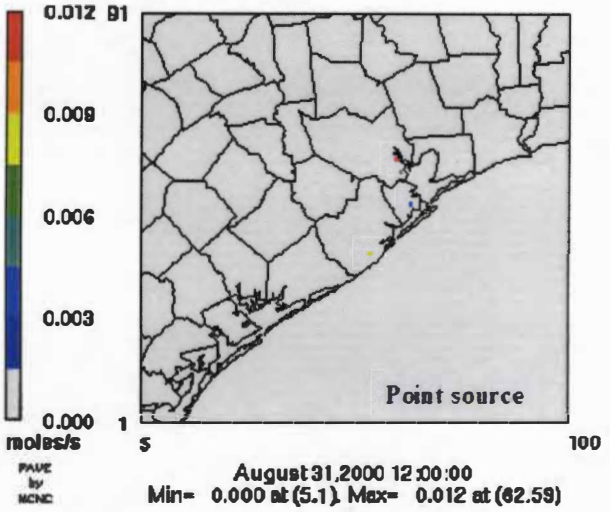


Figure 45 Chloroform Emissions Distribution





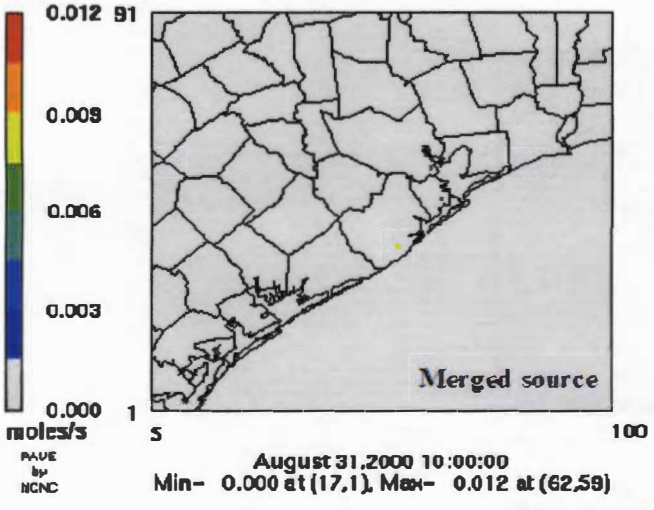
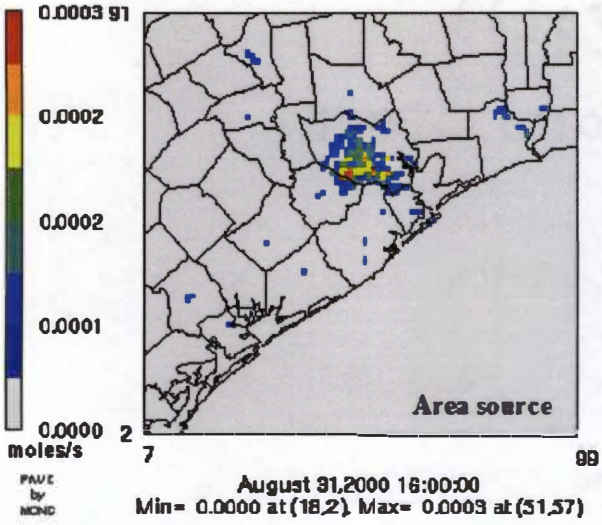
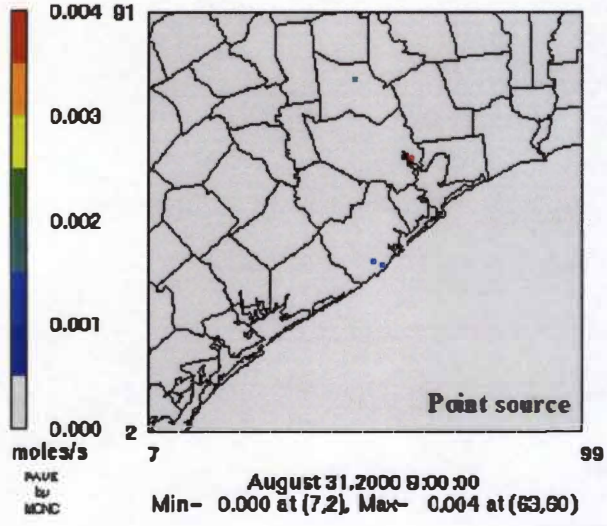


Figure 46 Vinyl Chloride Emissions Distribution





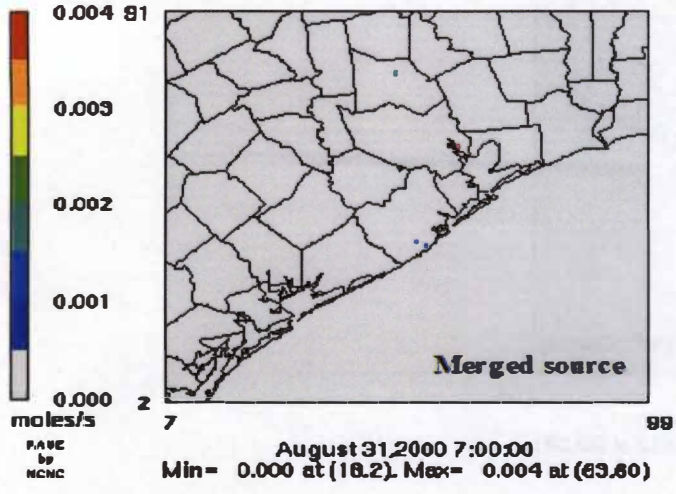
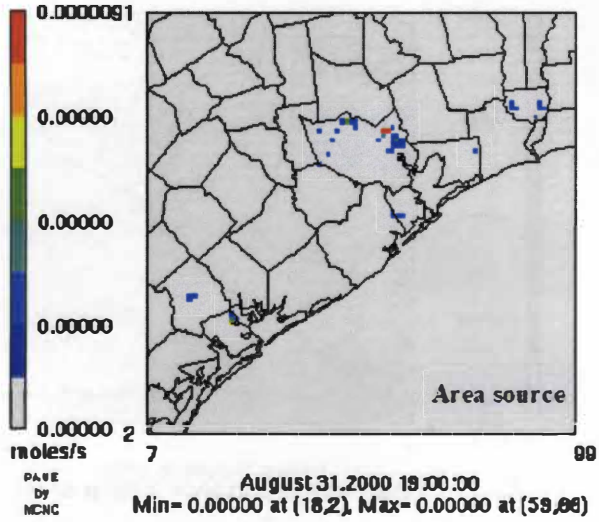
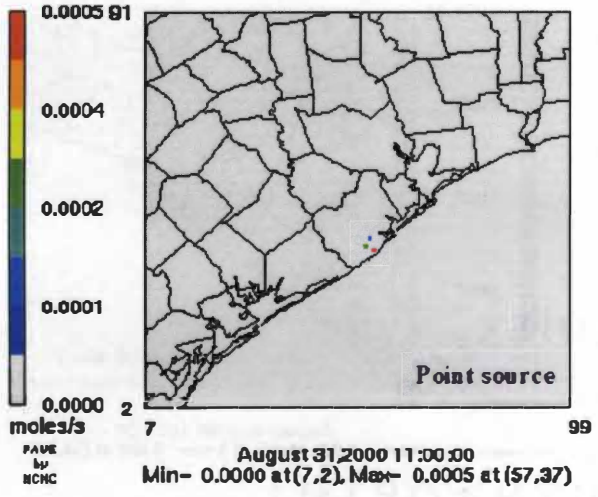


Figure 47 Trichloroethylene Emissions Distribution





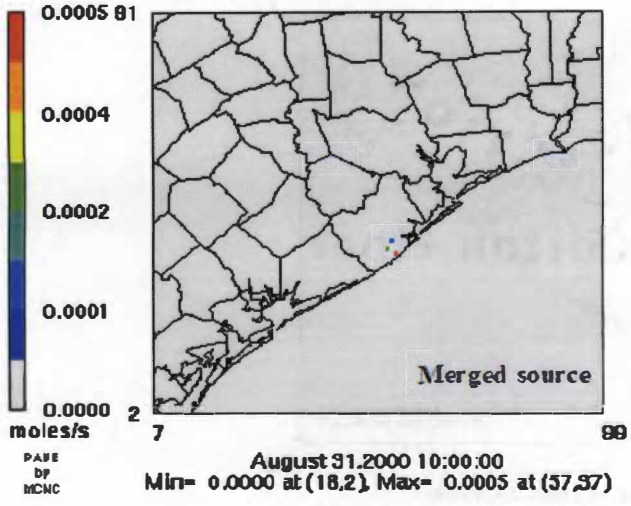


Figure 48 Propylene Dichloride Emissions Distribution

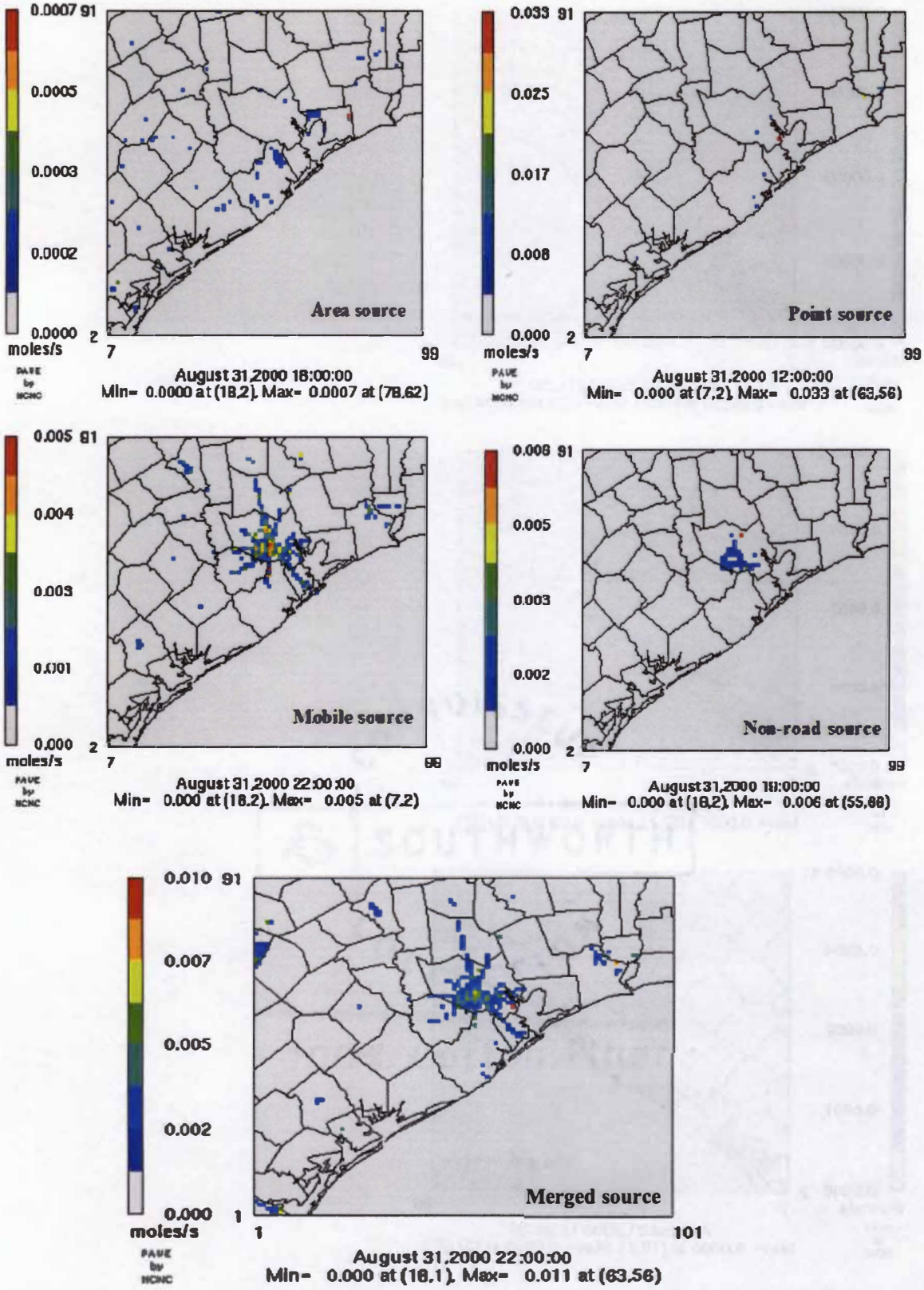


Figure 49 1,3 Butadiene Emissions Distribution

emissions can be observed in a number of counties present in the western side of the region Harris County is the chief contributor to the mobile source emission of butadiene. Harris County also emits a significant of acetaldehyde (Figure 50) and other aldehyde compounds. High emissions of mobile source aldehyde emissions can be observed in regions between Harris, Brazoria, Galveston, and Fort Bend Counties.

The results obtained from the percentage contribution of toxics emitted in the region on the basis of source are also presented in this section. From Figure 51 it can be observed that more than 60% of the total acrolein emissions in the state are emitted by area sources. Area sources also emit 50% of the total acetaldehyde emissions in the region. Mobile sources form almost 48% and 42% of total benzene and butadiene emissions respectively. 51% of acetaldehyde emissions and 93% of perchloroethylene emissions in the state of Texas are emitted by area sources. To bring significant reduction in the perchloroethylene emissions in the region, it is important to address the contribution of area sources.

From Figure 52 it can be observed that most of the vinyl chloride emissions in the state of Texas are emitted by point sources only. It can be also be found that point sources in the state of Texas contribute to 89% of ethylene dichloride emissions and around 57% of chloroform emissions in the state. 98% of acrylonitrile emissions and 94% of carbon tetrachloride emissions in the state are from point sources.

It can be concluded from the above observations that a decrease in point source emissions of acrylonitrile, ethylene dichloride, and carbon tetrachloride would bring a significant reduction in the total emission of these species in the state.

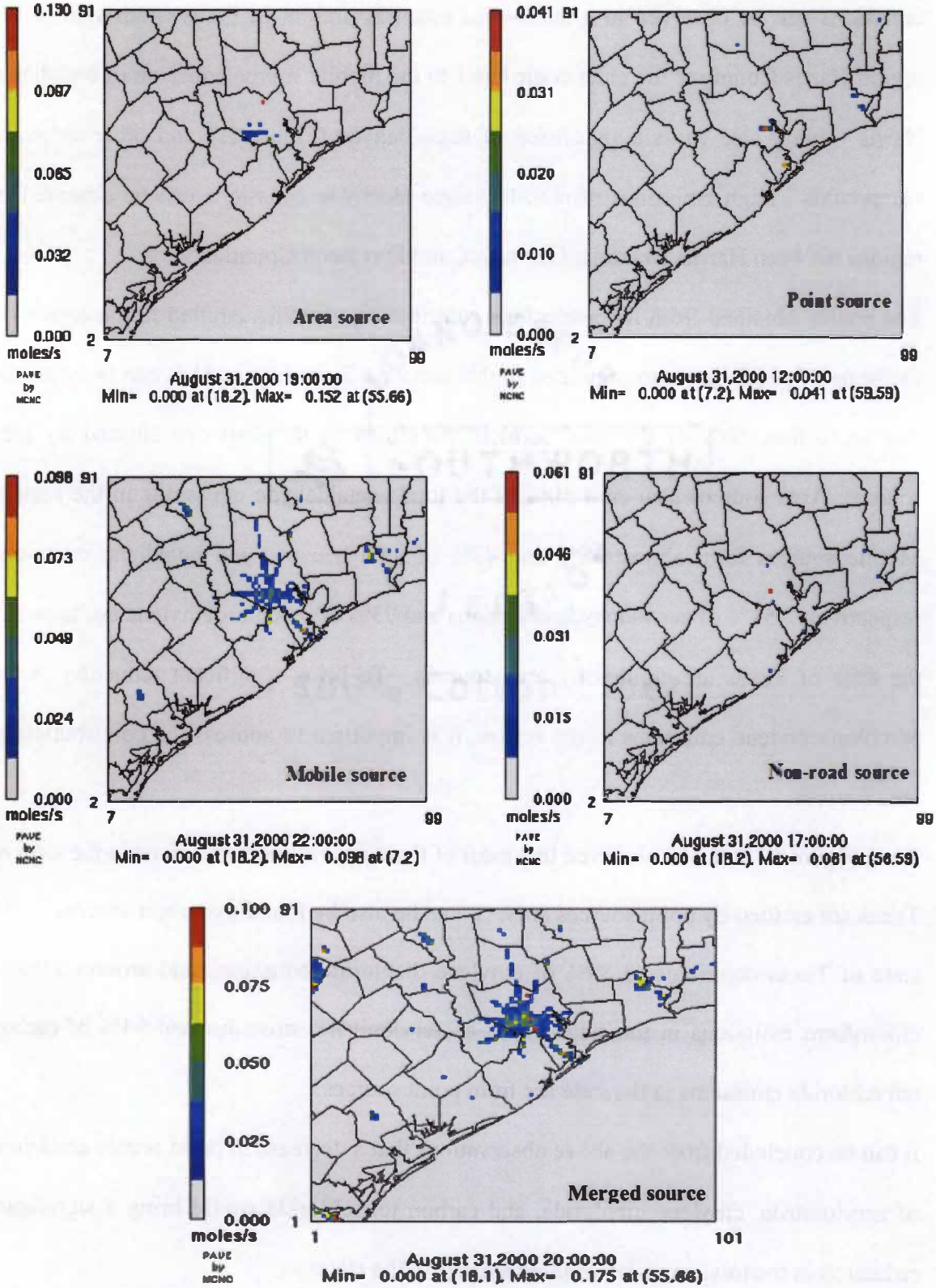


Figure 50 Aldehyde Emissions Distribution

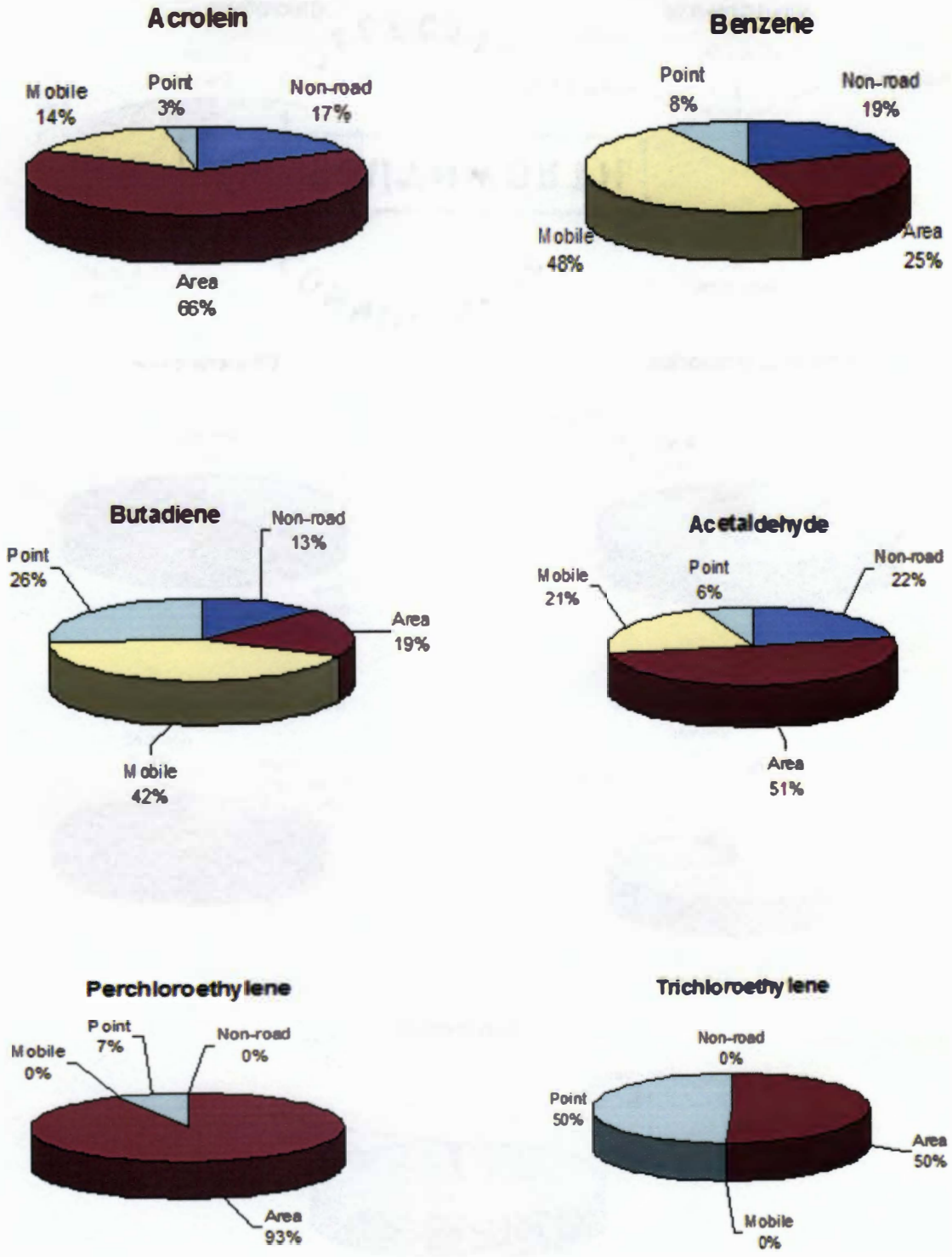


Figure 51 Percentage contributions of emissions by source I

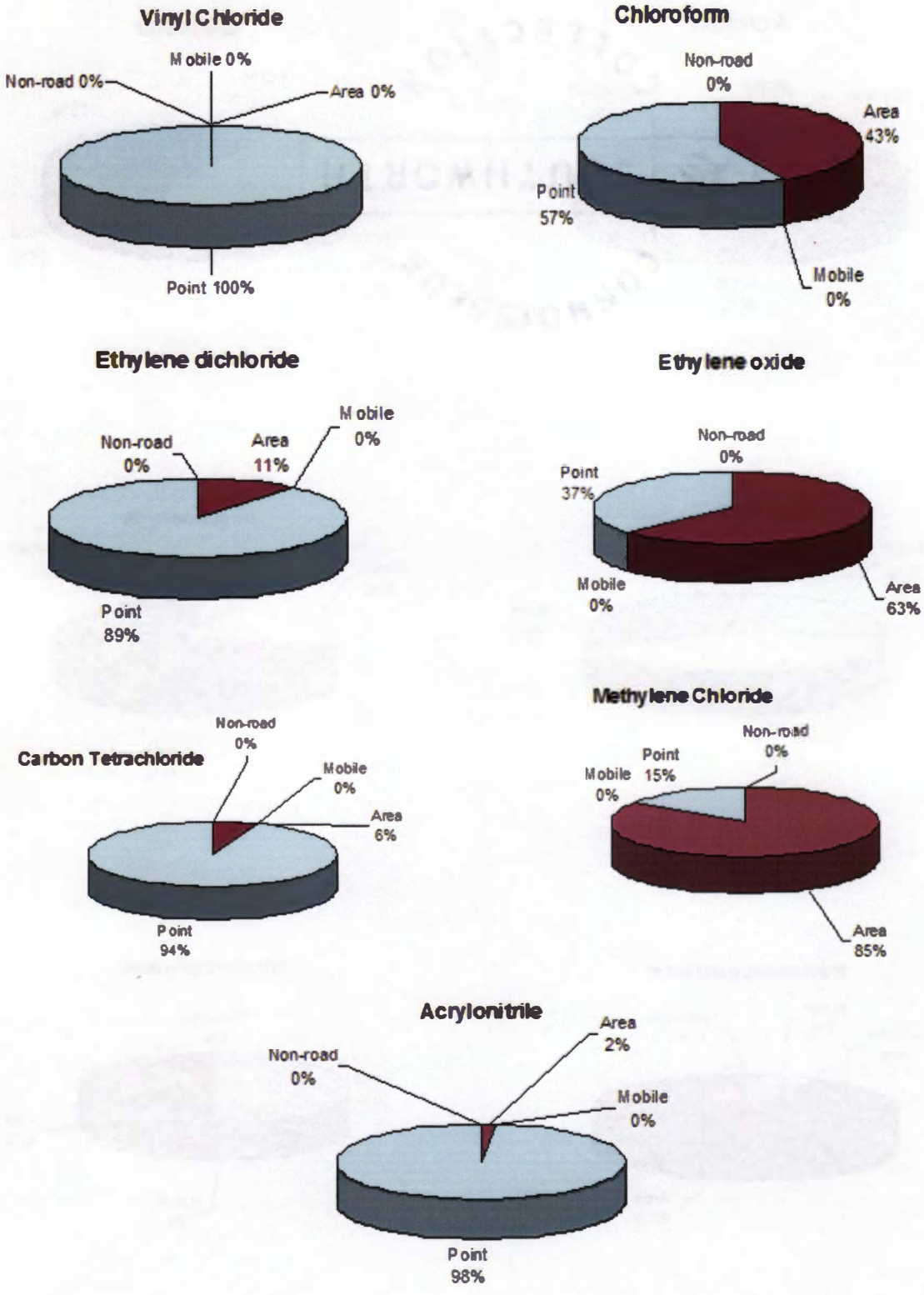


Figure 52 Percentage contributions of emissions by source II

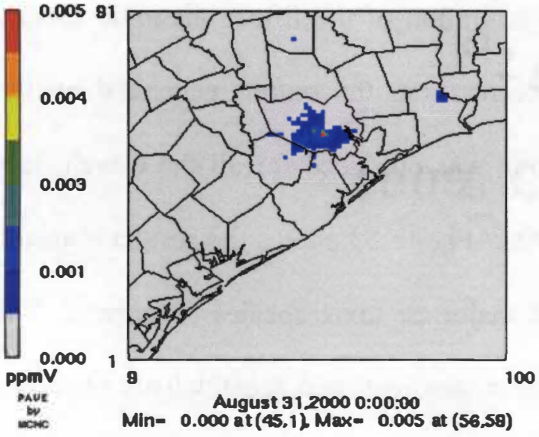
4.2 CMAQ air toxics model output

The CMAQ air toxic model predicted the concentration of the fifteen air toxic species considered in this thesis. To obtain the concentration, the output generated by the emission processor was used. The concentration was produced for all the eleven days starting from August 22nd to September 1st, 2000. Figure 53 shows the results obtained from CMAQ air toxics model for some of the major air toxic species considered. The Figure 53 represents the concentration of benzene, acrolein, and acetaldehyde observed on August 31st, 2000. It can be observed that at the start of the day considered benzene concentration in the region is largely confined to the Harris County, particularly around the Houston area, Texas.

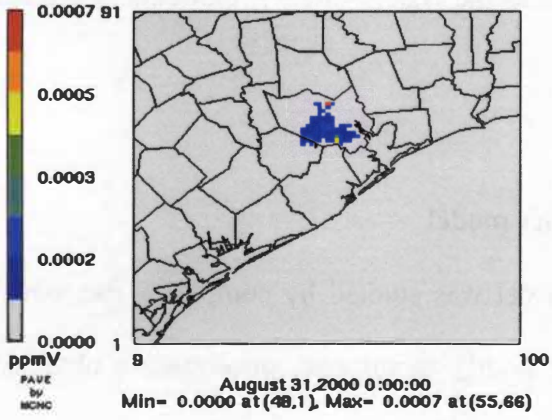
4.3 Performance Analysis of CMAQ air toxics model

The performance of the CMAQ air toxics model was studied by comparing the model predicted concentration of benzene with the hourly monitored concentration obtained from a monitoring station in the Harris County. Of the fifteen species modeled only benzene and acetaldehyde were selected for analysis as among the toxic species considered, the complete hourly monitoring data for all the days modeled were available for benzene and acetaldehyde only. The monitoring station data was provided by the TCEQ in Texas. The concentration measured by the station was compared with model predicted concentration at the station coordinates. As stated earlier the first few days concentration generated by the model was ignored and starting from August 27, 2000 the hourly concentration predicted by the model was compared with monitored values.

Benzene Concentration



Acrolein Concentration



Acetaldehyde Concentration

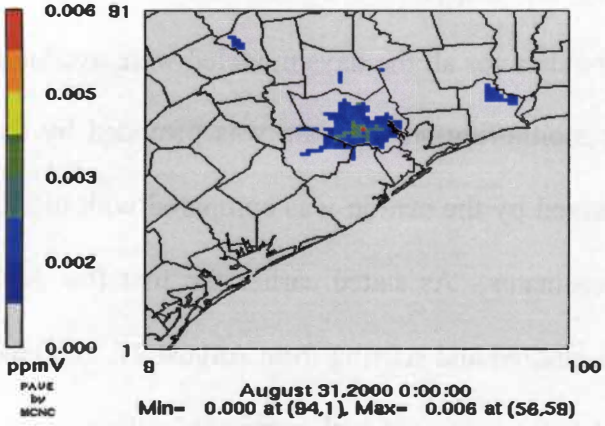
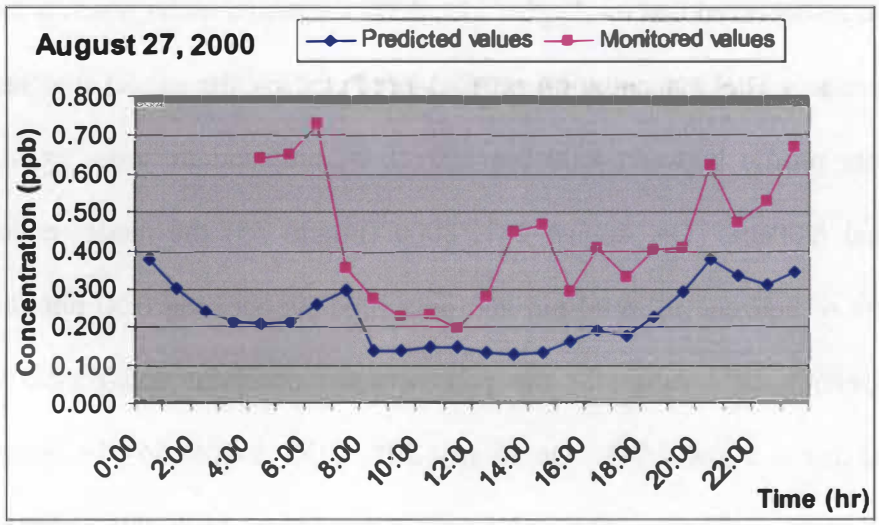
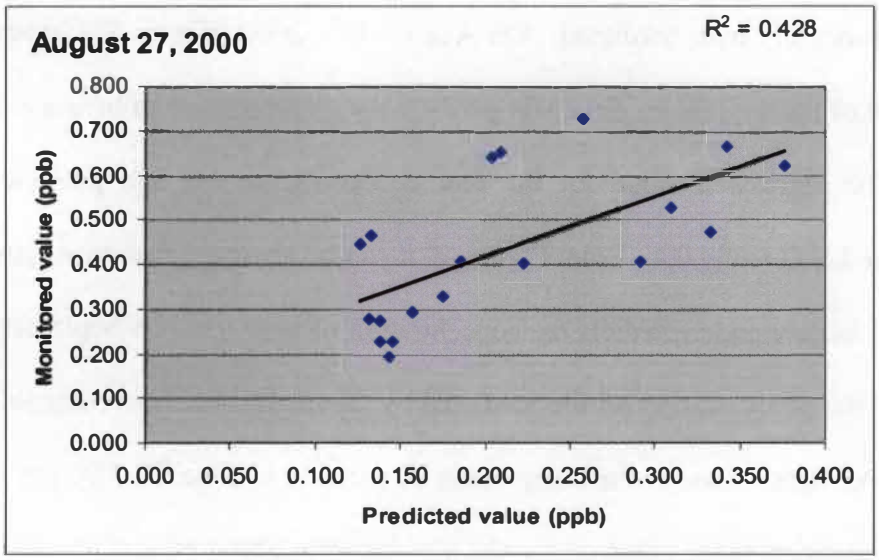


Figure 53 CMAQ output for major toxic species considered

From Figure 54 it can be observed that on August 27th, 2000 the model under predicts the concentration of benzene. The concentration profiles predicted by the model matches closely with real data profile between 8.00 pm and 10.00 pm, and to some extend between 6.00 am and 8.00am. On August 28th, 2000 (Figure 55) the model under predicts concentration of benzene till 6.00 pm and over predicts between 6.00 pm and 8.00 pm. The regression (R^2) value for the plot between observed and predicted concentration on that day is a low 0.585. On August 29th, 2000 (Figure 56) the model under predicts for almost the entire day, except between 9.00 pm and 11.00 pm when the concentration is significantly over predicted. On August 30th, 2000 (Figure 57) except for the last two hours of the day, the model under predicts the concentration of benzene in the atmosphere. The regression value for the plot between observed and predicted concentration on that day is really 0.4. From Figure 58 it can be observed that on August 31st, 2000 the model largely under predicts the concentration of benzene. On September 1st, 2000 (Figure 59) the concentration profile predicted by the model matches reasonably well with the real time data. Though the comparison of the data is done till 3.00 pm in the afternoon, the regression value obtained for the plot between observed and predicted concentration is good (0.73). A graph representing the overall comparison between predicted benzene concentration and measured benzene concentration, for the six days considered is shown in Figure 60. The acetaldehyde concentration predicted by the model was compared with monitored concentration for the date of August 30, 2000. Comparison of the predicted and monitored concentration for four different hours on that day is shown in Table C.1 of Appendix C. Figure 61 is a plot drawn between monitored and predicted acetaldehyde concentration.





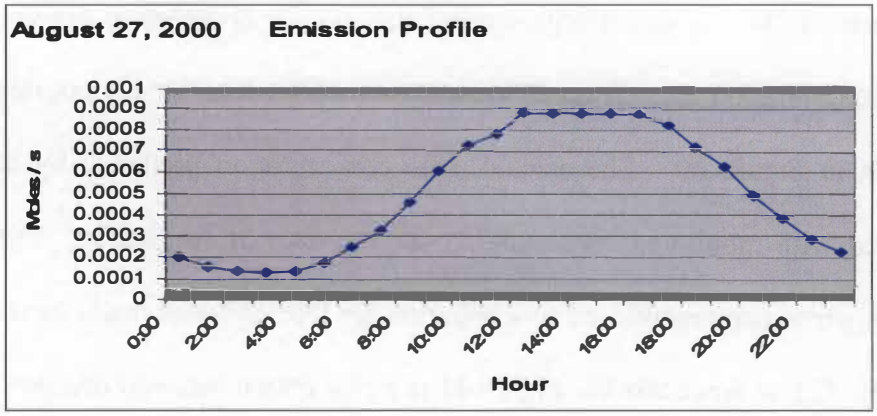
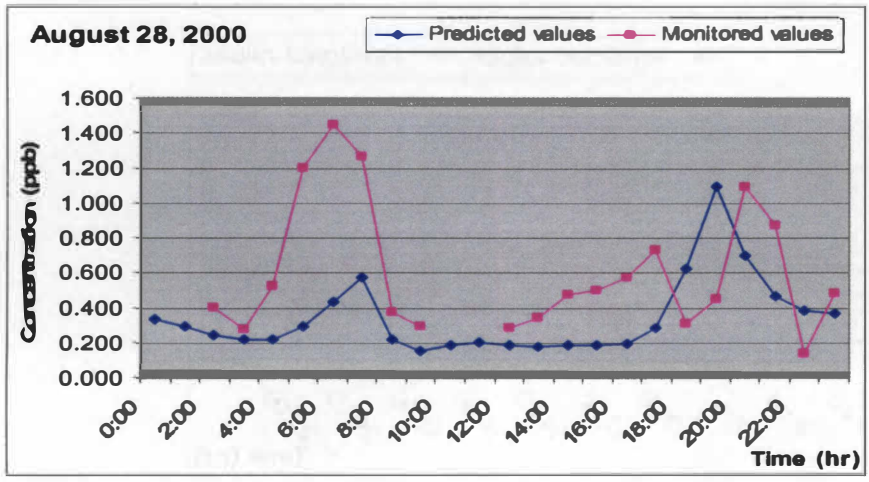
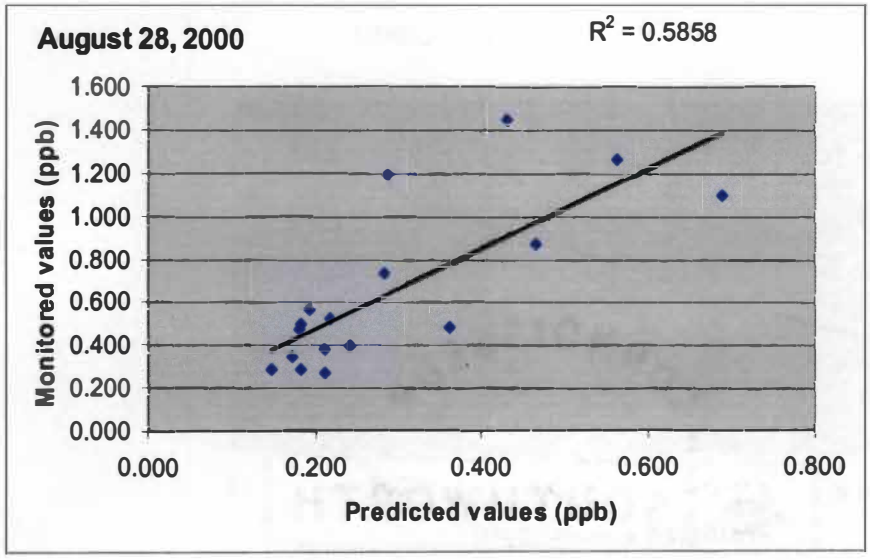


Figure 54 Comparison of predicted benzene concentration with measured values I





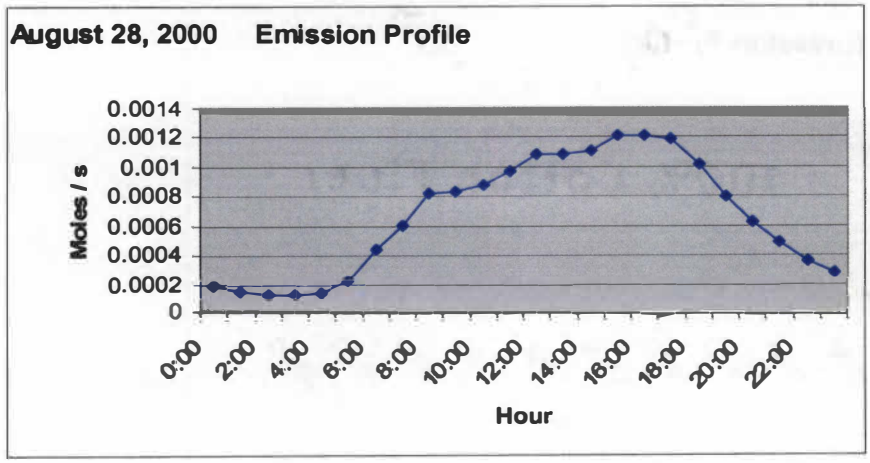
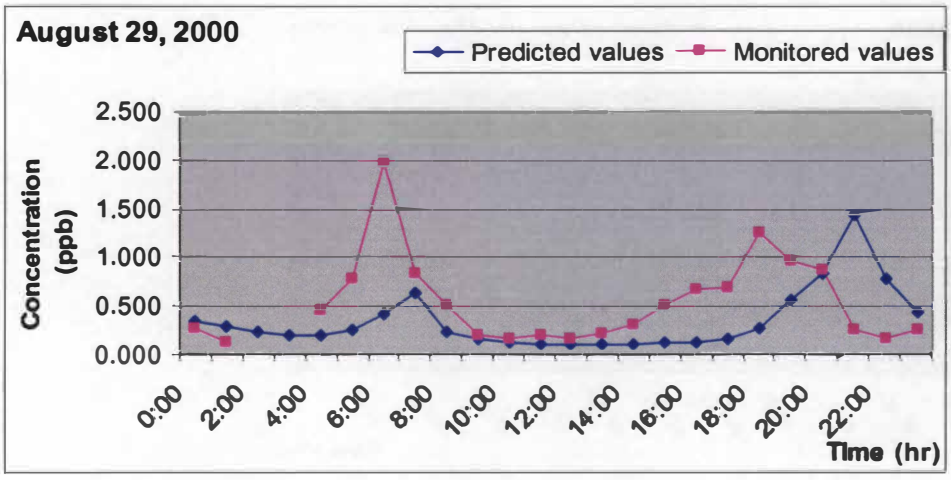
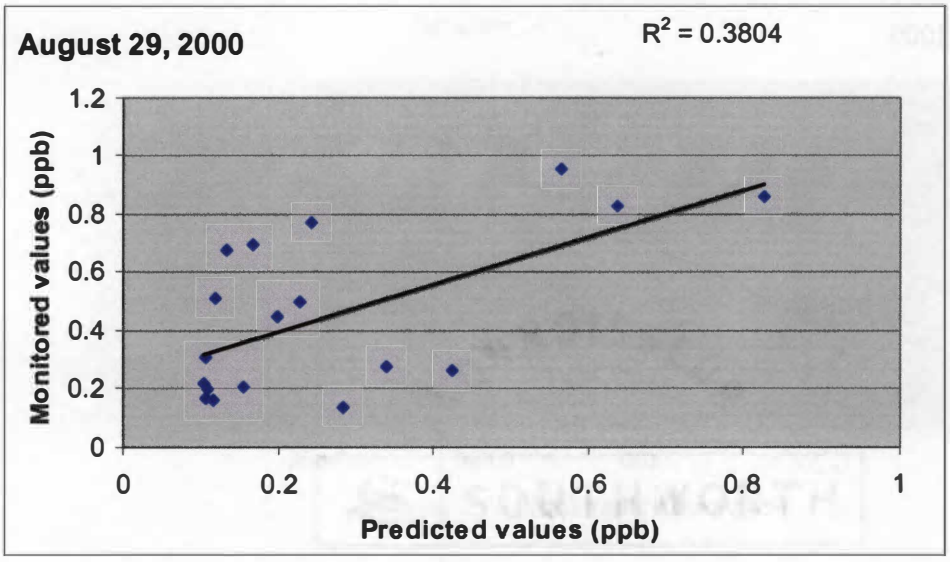


Figure 55 Comparison of predicted benzene concentration with measured values II





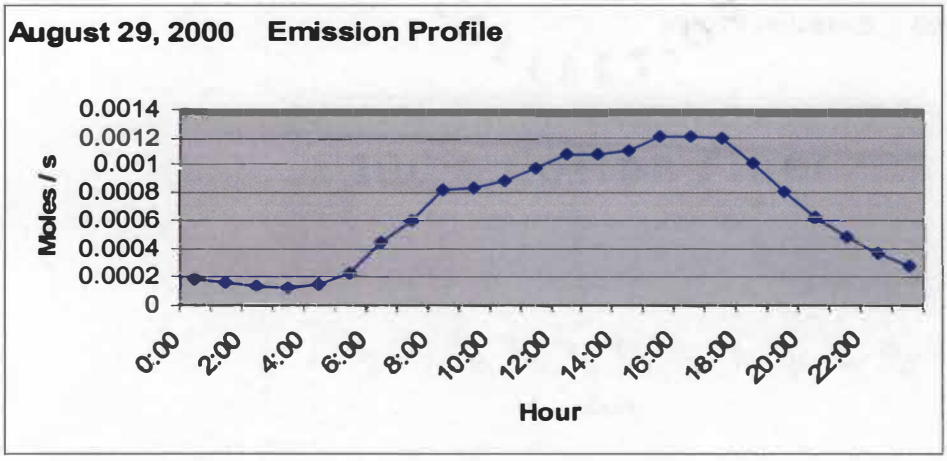
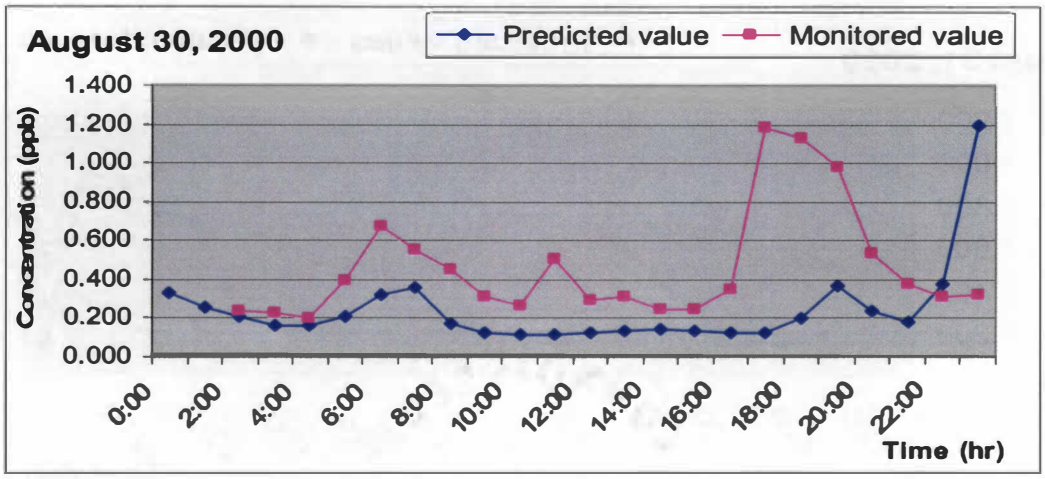
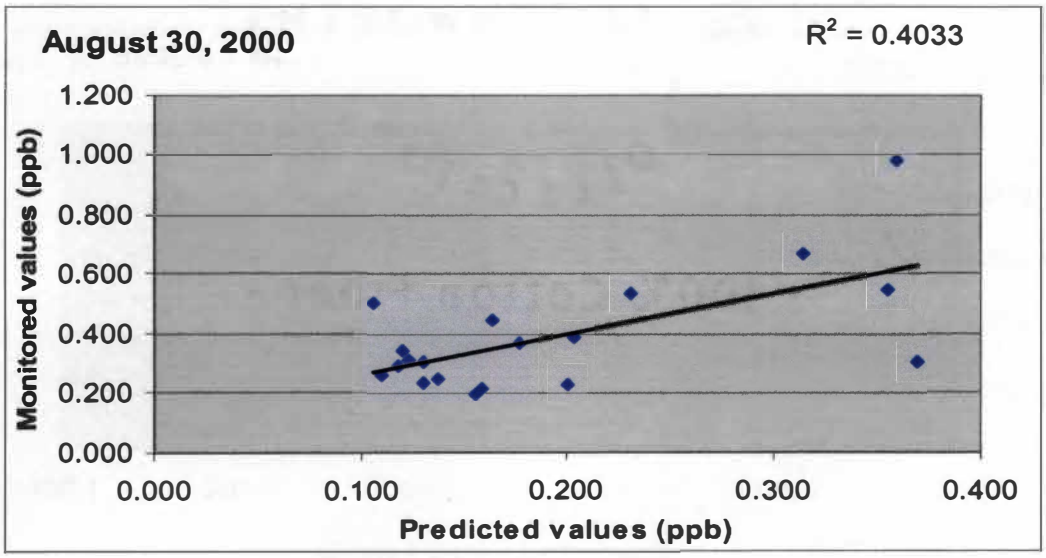


Figure 56 Comparison of predicted benzene concentration with measured values III





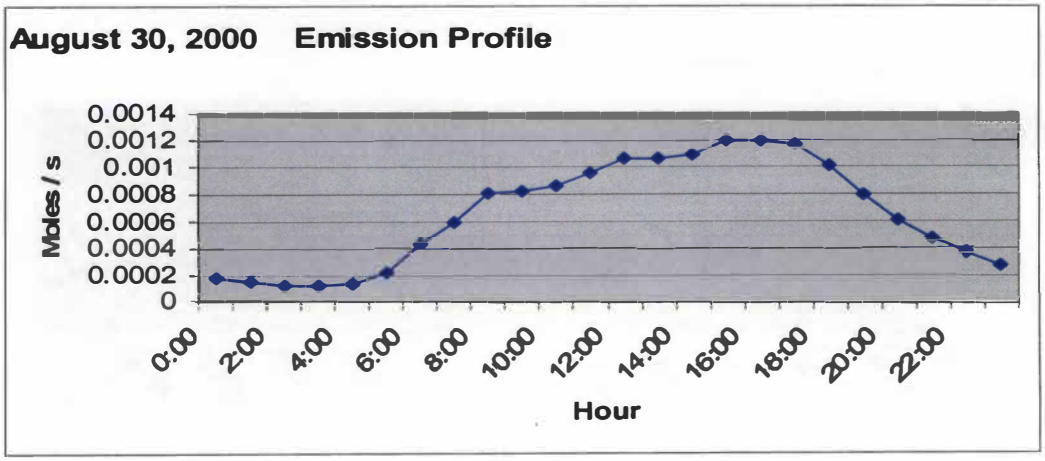


Figure 57 Comparison of predicted benzene concentration with measured values IV

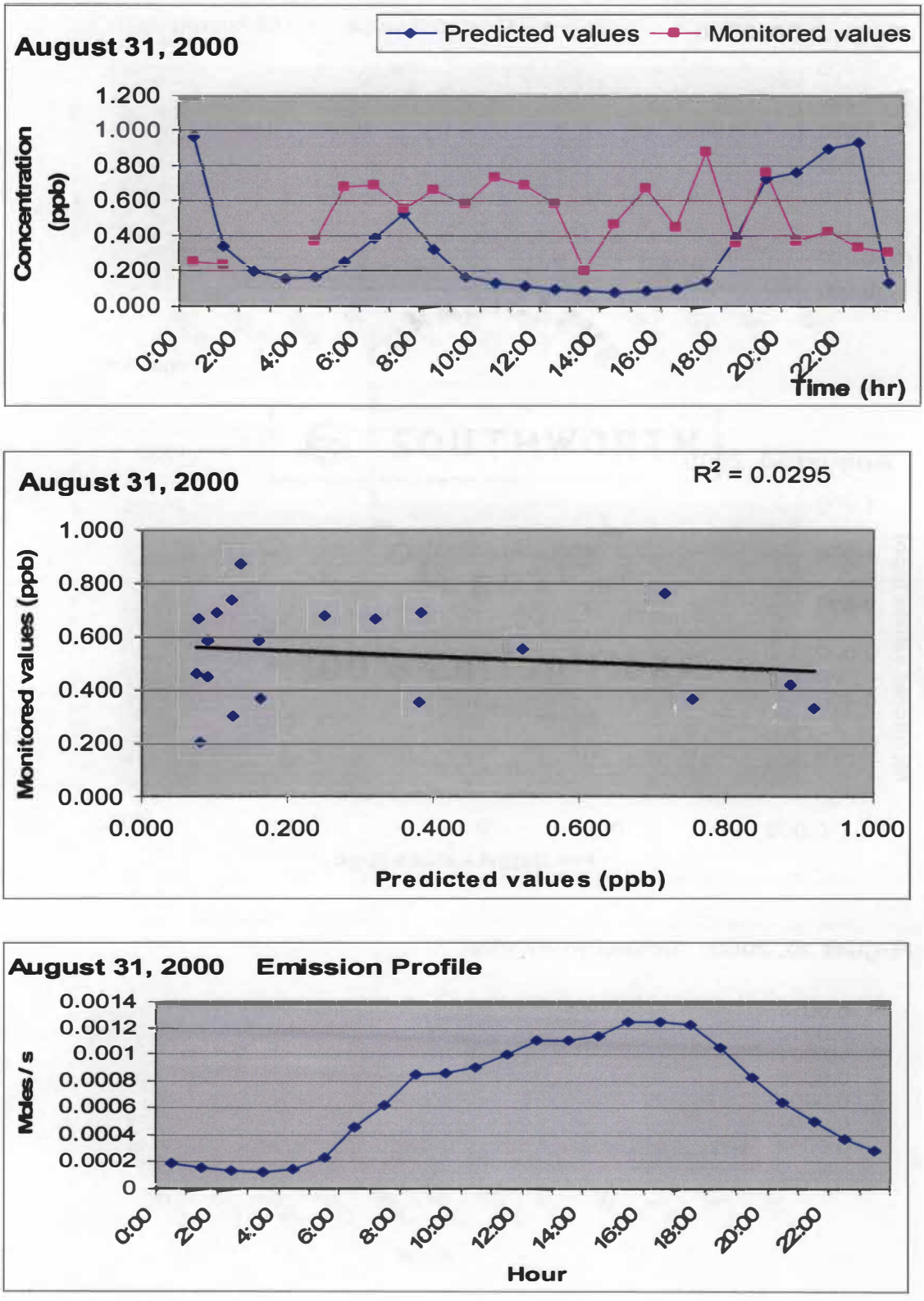
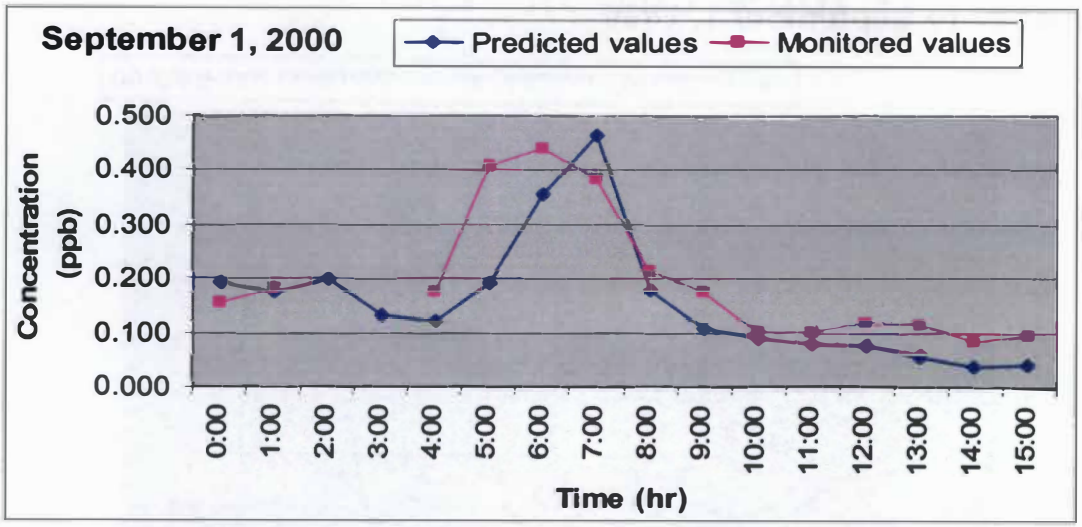
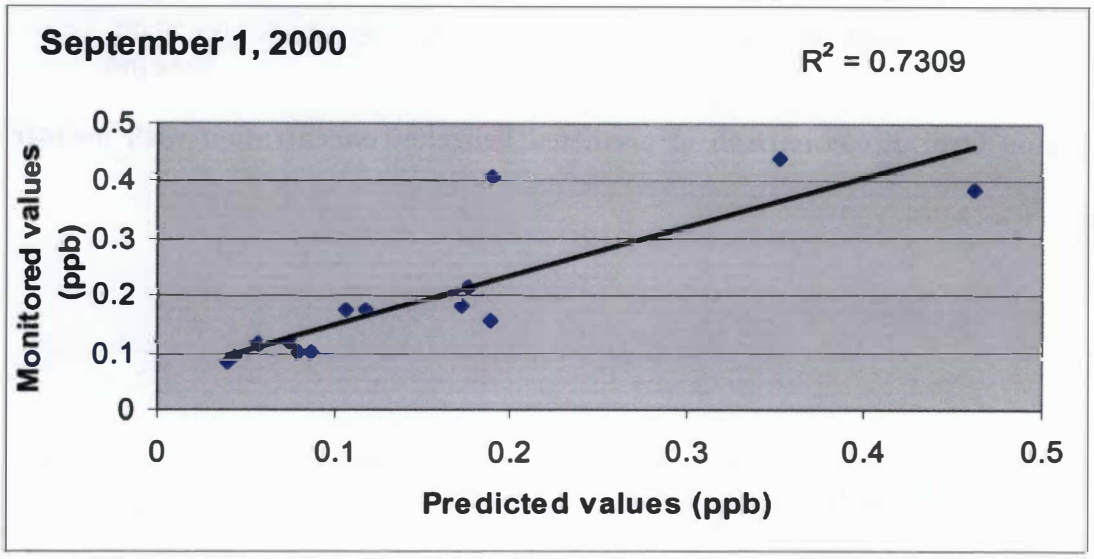


Figure 58 Comparison of predicted benzene concentration with measured values V





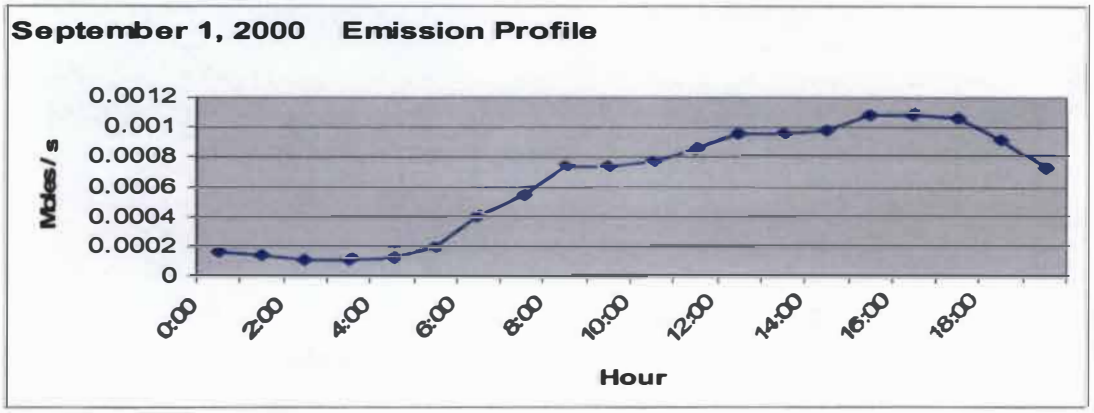


Figure 59 Comparison of predicted benzene concentration with measured values VI

August 27 to September 1, 2000

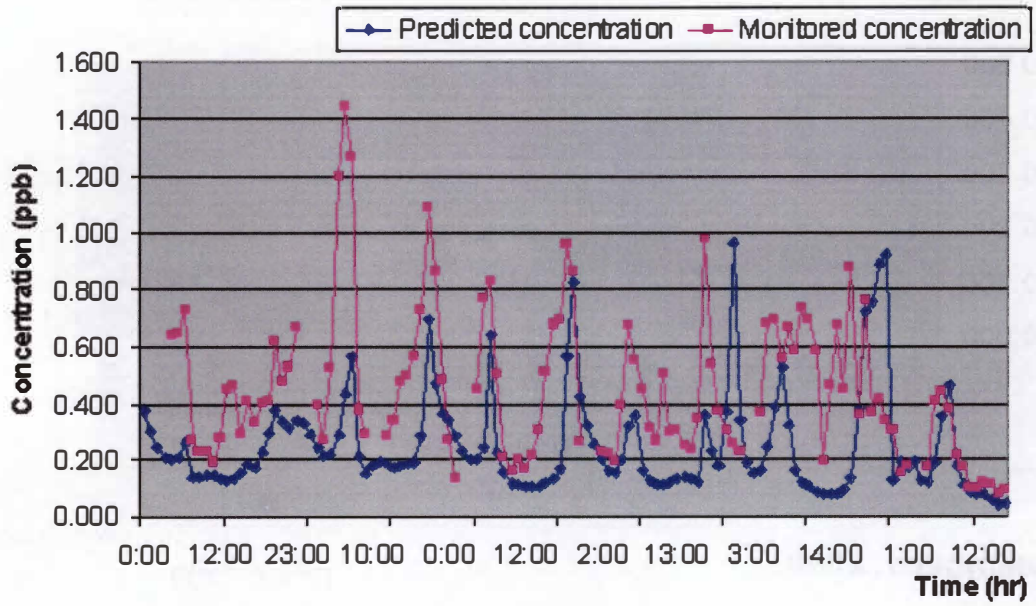


Figure 60 Overall comparison of predicted benzene concentration with measured values

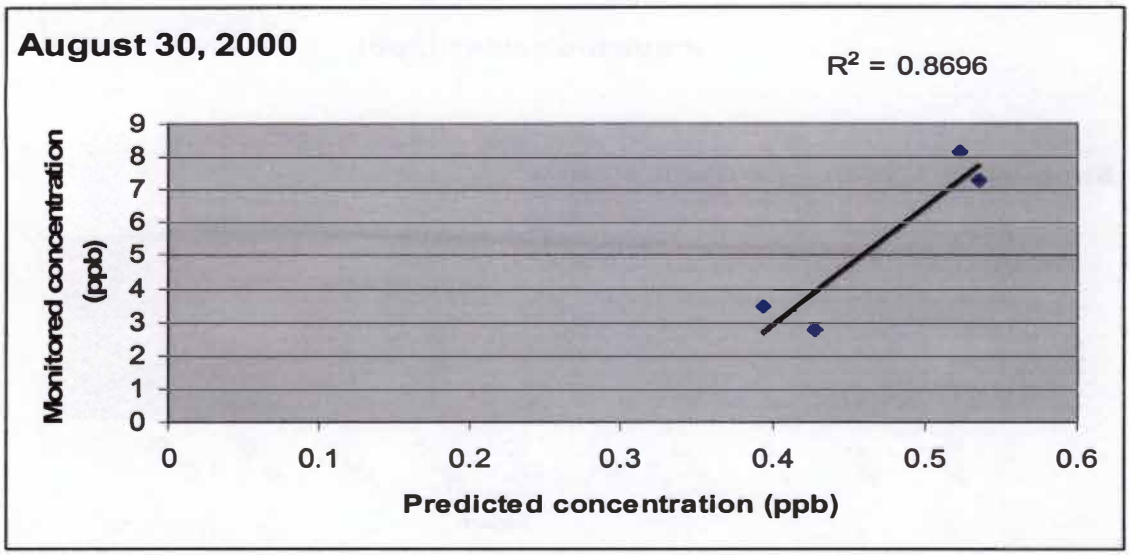


Figure 61 Monitored and predicted acetaldehyde concentration plot

CHAPTER 5

CONCLUSION

A detail analysis of the distribution of toxic emission in the Houston region was conducted. From the analysis it can be concluded that majority of air toxics in the region are emitted in Harris County. A decrease in Harris county emissions will significantly reduce the overall toxic emissions in the region. Potential reductions in toxic emissions can be identified on the basis of percentage contribution by source plots shown in the thesis. For example to achieve in a considerable decrease in the region's benzene emissions, the on-road mobile sources must be addressed. Almost 50% of the total benzene emissions are from on-road mobile sources and it is important to regulate emissions from this source in order to reduce the overall benzene emissions. A similar approach should be adopted for other toxic species. The performance of the CMAQ air toxics model was studied by comparing the hourly concentration of benzene and acetaldehyde predicted by the model with the concentration recorded by a monitoring station in the region. From the comparison it was observed that the model under predicts benzene concentration on a number of occasions and over predicts mostly towards the end of the day. A ratio between monitored benzene concentration and predicted benzene concentration gave an average value of 2.28. The possible reason for the difference between predicted and observed concentration could be the emission profiles generated by the emission processor used. Improving the accuracy of emission profile can offset some of the difference between predicted and monitored values. The difference can also be reduced by using a more comprehensive and accurate emission inventory. The

national emission inventory and the toxic release inventory is not exclusive, a number of emitting sources are not reported in these inventories. By developing a more accurate and comprehensive inventory the difference between predicted and monitored value can be reduced significantly. The under prediction in the acetaldehyde concentration could be due to the biogenic emission sources. In this thesis the primary focus was man made emissions and hence biogenic sources were not considered. Taking biogenic sources into account can reduce the difference in acetaldehyde concentration.

Disclaimer - The use of the term "mobile source" in this thesis solely refers to on-road mobile sources only.

REFERENCES

REFERENCES

- EPA - 452/K-00-002: *Taking Toxics out of the air*, US EPA Office of Air Quality Planning and Standards, 2000

- ATW (Air Toxics Website)-intro*: Technology Transfer Network, Air toxics website:* US EPA web page, 2004 www.epa.gov/ttn/atw/allabout.html

- Air-Trends'95: *AIR Trends 1995 summary*; US EPA webpage www.epa.gov/air/aqtrnd95/tap.html

- Arlene S. Rosenbaum, Daniel A.Axelrad and Tracey J. Woodruff, Yi-Hua Wei, Mary P.Ligocki, and Jonathan P. Cohen; *National Estimates of Outdoor Air Toxics Concentration* ISSN 1047-3289 .J AWMA 49: 1138-1152, 1999

- Winifred J.Hamilton; *Danger in the Air: Toxic Air Pollution in the Houston-Galveston Corridor*, 1996 www.ghasp.org/publications/toxics_report/overview.htm

- Air Trends 2003: *EPA AIR trends report* 2003 http://www.epa.gov/airtrends/toxic.html

- Hogrefe Christian, Gopal Sistla, Eric Zalewsky, Winston Hao, and Jia-Yeong Ku; *An Assessment of the Emissions Inventory Processing Systems EMS-2001 and SMOKE in Grid-Based Air Quality Models* .J AWMA 1047-3289, 2003.

- Benjey William, Houyoux Marc, and Susick Joseph; *Implementation of the SMOKE Emission Data Processor and SMOKE Tool Input Data Processor in Models-3*; EPA Emission Inventory Conference 2002

- SMOKE manual, 2003 - *SMOKE user manuals and other documentation*; 2003 Carolina Environmental Program

- Houyoux Marc and Vukovich Jeffrey; *Update to Sparse Matrix Operator Kernel Emissions (SMOKE) Modeling System and Integration with Models-3, 1999*; MCNC, NC

- SCRAM user guide – *Support Center for Regulatory Air Models* EMS-HAP, 2002 http://www.epa.gov/scram001/userg/other/emshapdescv2.pdf

- SCRAM001, uamz6 – *Support Center for Regulatory Air Models* EPS 2.0, 1992 http://www.epa.gov/scram001/mcbs/uamz6.txt

- APCD: *Air Pollution Control District – Santa Barbara,* 2004 http://www.sbcapcd.org/biz/modeling.htm
- *Mid-Atlantic Air Protection – Air Quality Modeling,* 2003 http://www.epa.gov/reg3artd/airquality/mod.htm
- *NILU – Norwegian Institute for Air Research,* 2001 http://www.nilu.no/AQM/1d_use_of%20ap_models.htm
- MPCA 2/16/01: *Minnesota Pollution Control Agency –air toxics* 2001 http://www.pca.state.mn.us/hot/legislature/reports/2001/at-appendix-d.pdf
- ATW- Urban, 2004 - http://www.epa.gov/ttn/atw/urban/list33.html
- Health Effect Notebook for Hazardous Air Pollutants 2004 http://www.epa.gov/ttn/atw/hapindex.html
- ATW- Pollutants and sources, 2004 http://www.epa.gov/ttn/atw/pollsour.html
- CDEP - Connecticut Department of Environmental Protection, 1999 http://dep.state.ct.us/air2/toxics/sources.htm
- EPA-OTAQ – *Mobile source emissions,* 2003 http://www.epa.gov/otaq/invntory/overview/examples.htm
- NEI background, 2004; http://www.epa.gov/ttn/chief/net/neiwhatis.html
- EPA's *NEI point source documentation,* 2004; http://www.epa.gov/ttn/chief/net/1999inventory.html#final3haps
- EPA's *NEI Mobile source documentation,* 2004
- EPA's *NEI Area source documentation,* 2004
- TRI 2000; *Toxic Release Inventory Executive summary* 2000
- Air trends report 2003
- Ching Jason and Byun Daewon; *Introduction to Models3 framework and the community multiscale air quality model (CMAQ);* EPA/600/R-99/030 -2003
- Seigneur Christian, Lohman Kristen, and Pun Betty; *Critical review of air toxics modeling current status and key issues*; CRC August 2002

- Roselle Shawn, Schere Kenneth, and Pleim Jonathan; *Photolysis Rates for CMAQ*; EPA/600/R-99/030-2003

- Byun Daewon, Young Jeffery, and Pleim Jonathan; *Numerical transport algorithms for the community multiscale air quality (CMAQ) chemical transport model in generalized coordinate*; EPA/600/R-99/030 - 2003

- Gipson Gerald; *The initial concentration and boundary concentration processors*; EPA/600/R-99/030-2003

- Gipson Jerry; *A photochemical Kinetics Mechanism for Urban and Regional Scale Computer Modeling*; JGR, 9/89

- GHASP, *How bad is Houston's Smog?* Houston leads Nation in Exposures to Ozone smog, 2002

- GHASP 2003; *Where does Houston's smog come from?* Twenty more answers, further data and technical background

- GHASP October 2003; *where does Houston's smog come from?* The sources of Houston's Air Pollution and What's Needed to clear the air

- *Texas Air Quality Study 2000*; University of Texas, http://www.utexas.edu/research/ceer/texaqs/participants/photos/

- Brown Steven, Reid Steven, Roberts Paul, Buhr Martin, and Funk Tami; *Reconciliation of the VOC and NOx Emission Inventory with Ambient Data in the Houston, Texas Region*; 2004

- MCM 2004– *The Master Chemical Mechanism website*, The University of Leeds

APPENDICES

APPENDIX A

MONITORED AND PREDICTED CONCENTRATION OF BENZENE BETWEEN AUGUST 27TH AND SEPTEMBER 1ST, 2000

Table A.1 Comparison of benzene concentration on August 27th, 2000

Date	Time (hr)	Predicted value (ppb)	Monitored value (ppb)	Monitored value / Predicted value
August 27, 2000	0:00	0.376	X	
	1:00	0.300	X	
	2:00	0.240	X	
	3:00	0.210	X	
	4:00	0.204	0.638	3.13
	5:00	0.209	0.647	3.10
	6:00	0.257	0.725	2.82
	7:00	0.294	0.353	1.20
	8:00	0.138	0.270	1.96
	9:00	0.138	0.225	1.63
	10:00	0.146	0.227	1.55
	11:00	0.144	0.190	1.32
	12:00	0.132	0.277	2.10
	13:00	0.127	0.443	3.49
	14:00	0.133	0.462	3.47
	15:00	0.157	0.290	1.85
	16:00	0.186	0.403	2.17
	17:00	0.175	0.327	1.87
	18:00	0.223	0.400	1.79
	19:00	0.291	0.402	1.38
	20:00	0.376	0.618	1.64
	21:00	0.332	0.470	1.42
	22:00	0.309	0.525	1.70
	23:00	0.342	0.662	1.94

Note: X refers to data not available

Table A.2 Comparison of benzene concentration on August 28th, 2000

Date	Time (hr)	Predicted value (ppb)	Monitored value (ppb)	Monitored value / Predicted value
August 28, 2000	0:00	0.330	X	
	1:00	0.286	X	
	2:00	0.243	0.393	1.62
	3:00	0.212	0.270	1.27
	4:00	0.217	0.517	2.38
	5:00	0.288	1.193	4.14
	6:00	0.431	1.440	3.34
	7:00	0.565	1.260	2.23
	8:00	0.211	0.375	1.78
	9:00	0.147	0.287	1.95
	10:00	0.178	X	
	11:00	0.195	X	
	12:00	0.183	0.283	1.55
	13:00	0.172	0.342	1.99
	14:00	0.181	0.470	2.60
	15:00	0.183	0.497	2.72
	16:00	0.192	0.565	2.94
	17:00	0.283	0.725	2.56
	18:00	0.619	0.307	0.50
	19:00	1.090	0.447	0.41
	20:00	0.690	1.088	1.58
	21:00	0.465	0.865	1.86
	22:00	0.379	0.132	0.35
	23:00	0.360	0.475	1.32

Note: X refers to data not available

Table A.3 Comparison of benzene concentration on August 29th, 2000

Date	Time (hr)	Predicted value (ppb)	Monitored value (ppb)	Monitored value / Predicted value
August 29, 2000	0:00	0.339	0.273	0.81
	1:00	0.284	0.133	0.47
	2:00	0.228	X	
	3:00	0.199	X	
	4:00	0.199	0.445	2.24
	5:00	0.243	0.767	3.16
	6:00	0.405	1.963	4.85
	7:00	0.636	0.828	1.30
	8:00	0.227	0.498	2.19
	9:00	0.155	0.205	1.32
	10:00	0.117	0.160	1.37
	11:00	0.109	0.200	1.83
	12:00	0.106	0.167	1.58
	13:00	0.104	0.215	2.07
	14:00	0.106	0.305	2.88
	15:00	0.118	0.505	4.28
	16:00	0.134	0.673	5.02
	17:00	0.166	0.692	4.17
	18:00	0.272	1.243	4.57
	19:00	0.565	0.953	1.69
	20:00	0.825	0.858	1.04
	21:00	1.414	0.258	0.18
	22:00	0.778	0.160	0.21
	23:00	0.423	0.260	0.61

Note: X refers to data not available

Table A.4 Comparison of benzene concentration on August 30th, 2000

Date	Time (hr)	Predicted value (ppb)	Monitored value (ppb)	Monitored value / Predicted value
August 30, 2000	0:00	0.322	X	
	1:00	0.253	X	
	2:00	0.201	0.230	1.14
	3:00	0.159	0.218	1.37
	4:00	0.156	0.197	1.26
	5:00	0.204	0.390	1.91
	6:00	0.315	0.668	2.12
	7:00	0.355	0.547	1.54
	8:00	0.164	0.443	2.70
	9:00	0.124	0.308	2.48
	10:00	0.111	0.262	2.36
	11:00	0.107	0.500	4.67
	12:00	0.119	0.292	2.45
	13:00	0.131	0.307	2.34
	14:00	0.138	0.245	1.78
	15:00	0.131	0.238	1.82
	16:00	0.121	0.343	2.83
	17:00	0.116	1.182	10.19
	18:00	0.198	1.120	5.66
	19:00	0.359	0.978	2.72
	20:00	0.231	0.533	2.31
	21:00	0.178	0.370	2.08
	22:00	0.370	0.307	0.83
	23:00	1.189	0.315	0.26

Note: X refers to data not available

Table A.5 Comparison of benzene concentration on August 31st, 2000

Date	Time (hr)	Predicted value (ppb)	Monitored value (ppb)	Monitored value / Predicted value
August 31, 2000	0:00	0.962	0.253	0.26
	1:00	0.339	0.233	0.69
	2:00	0.192	X	
	3:00	0.147	X	
	4:00	0.163	0.365	2.24
	5:00	0.250	0.677	2.71
	6:00	0.383	0.688	1.80
	7:00	0.523	0.553	1.06
	8:00	0.321	0.662	2.06
	9:00	0.160	0.580	3.63
	10:00	0.123	0.733	5.96
	11:00	0.103	0.688	6.68
	12:00	0.089	0.580	6.52
	13:00	0.080	0.198	2.48
	14:00	0.075	0.458	6.11
	15:00	0.077	0.665	8.64
	16:00	0.091	0.445	4.89
	17:00	0.135	0.873	6.47
	18:00	0.381	0.355	0.93
	19:00	0.717	0.760	1.06
	20:00	0.754	0.365	0.48
	21:00	0.888	0.417	0.47
	22:00	0.921	0.332	0.36
	23:00	0.125	0.300	2.40

Note: X refers to data not available

Table A.6 Comparison of benzene concentration on September 1st, 2000

Date	Time (hr)	Predicted value (ppb)	Monitored value (ppb)	Monitored value / Predicted value
September 1, 2000	0:00	0.189	0.152	0.80
	1:00	0.172	0.180	1.05
	2:00	0.198	X	
	3:00	0.129	X	
	4:00	0.118	0.172	1.46
	5:00	0.190	0.405	2.13
	6:00	0.352	0.437	1.24
	7:00	0.462	0.382	0.83
	8:00	0.176	0.213	1.21
	9:00	0.107	0.172	1.61
	10:00	0.087	0.097	1.11
	11:00	0.079	0.097	1.23
	12:00	0.074	0.115	1.55
	13:00	0.057	0.112	1.96
	14:00	0.040	0.080	2.00
	15:00	0.044	0.092	2.09

Note: X refers to data not available

APPENDIX B

TOXIC CHEMICAL REACTIONS INCLUDED IN THE CMAQ AIR TOXIC MODEL

ACROLEIN + OH → 0.709 * FORM + 0.709 * ALD2_SUR + 0.709 * XO2
+ 0.709 * HO2 - 0.709 * PAR + 0.814 * C2O3

ACROLEIN + NO3 → 1.192 * XO2 + 0.118 * XO2N + 1.310*FORM
+ 1.310*ALD2_SUR - 1.310*PAR + 1.310*NO2
+ 0.851*C2O3 + 0.851*HNO3

ACROLEIN + O → 0.538 * ALD2_SUR + 0.325 * HO2
+ 0.239 * XO2 + 0.257 * CO + 0.171 * FORM
+ 0.017 * XO2N + 0.188 * PAR + 0.356 * OH
+ 0.185*C2O3

ACROLEIN → 6.3 * XO2 + 12.6 * HO2 + 6.3 * CO + 6.3 * FORM

BUTADIENE13 + OH → 0.85 * FORM + 0.85 * ACROLEIN
+ 0.85 * XO2 + 0.85 * HO2 - 0.85 * PAR

BUTADIENE13 + O3 → 0.50 * ACROLEIN + 2.81 * FORM + 1.26 * CO
+ 1.67 * HO2 + 0.84 * XO2 + 0.38 * OH
+ 0.76 * FACD (formic acid) + 0.76 * AACD (acetic acid)
- 3.8 * PAR

BUTADIENE13 + NO3 → 0.140 * XO2 + 0.014 * XO2N + 0.154 * FORM
+ 0.154 * ALD2_SUR - 0.154 * PAR + 0.154 * NO2

BUTADIENE13 + O → 0.230 * ACROLEIN + 0.155 * HO2 + 0.115 * XO2
+ 0.123 * CO + 0.082 * FORM + 0.008 * XO2N
+ 0.090 * PAR + 0.082 * OH

ALD2_SUR (secondary aldehyde) + O → C2O3 + OH

ALD2_SUR (secondary aldehyde) + OH → C2O3

ALD2_SUR (secondary aldehyde) + NO3 → C2O3 + HNO3

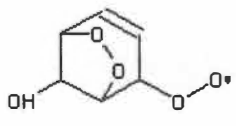
ALD2_SUR (secondary aldehyde) → XO2 + 2 * HO2 + CO + FORM

FORM_SUR (secondary formaldehyde) + OH → HO2 + CO

FORM_SUR (secondary formaldehyde) → 2 * HO2 + CO

FORM_SUR (secondary formaldehyde) + O → OH + HO2 + CO

FORM_SUR (secondary formaldehyde) + NO3 → HNO3 + HO2 + CO

BENZENE + OH → 

(BZIPERO2)

APPENDIX C

MONITORED AND PREDICTED CONCENTRATION OF ACETALDEHYDE ON AUGUST 30TH, 2000

Table C.1 Comparison of acetaldehyde concentration on August 30th, 2000

Day	Time (hr)	Predicted Concentration (ppb)	Monitored Concentration (ppb)
August 30, 2000	6.00	0.524	8.109
	7.00	0.536	7.226
	13.00	0.394	3.455
	14.00	2.75	6.425

VITA

Ramesh Ramachandran Gopal was born in Vellore, India on November 26th, 1979. He was raised in Madras (India) and graduated from high school in 1997. After obtaining his B.Tech degree in Chemical Engineering from the University of Madras (India) in April 2001, he joined a refinery company called Nagarjuna Oil Corporation Limited as an Engineer Trainee. In April 2002 Ramesh decided to continue his education and was accepted in to the environmental engineering graduate school at the University of Tennessee, Knoxville. Ramesh shall receive his M.S. in the Summer of 2004 in environmental engineering with concentrations in air quality and waste management.